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THE NATURE OF SECONDARY VALENCE

DISSERTATION

Submitted to the School of Hygiene and Public Health of
the Johns Hopkins University in Conformity with
the Requirements for the Degree of Doctor
of Science in ~~Public Health~~.

Homer W. Smith.
March 1921

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Biography.

Brief: It is within the province of this research to make use of a new method for the study of the intermolecular forces which are involved in the phenomena of solution; to show through the results obtained that molecular behavior is independent of the mass of the molecule, and equally independent of the hypothetical configuration which we ascribe to various molecular species in accounting for their chemical behavior; to show further that molecular behavior is conditioned by a limited number of variables, first of which is molecular volume, and second, the characteristic intensity of secondary valence. The former, molecular volume, is an independent variable, while the latter is dependent on the atomic or electronic fabrication of the molecule, and it is also subject to the external influences of environment. It has been found that secondary valence is discontinuous or rhythmic in nature, in that it can vary in intensity in different molecular species only by definite and integrally related amounts. The fundamental nature of these integral relationships in secondary valence is entirely independent of the atomic or molecular species under consideration. Consequently they cannot be attributed to peculiarities in atomic or molecular structure, but must be attributed to something common to all atomic species and more fundamental than atomic structure itself. It is held that they represent the intimate behavior of the fundamental electric charges, - that the rhythmic or discontinuous nature of the intermolecular forces is attributable directly to a similar discontinuity in the forces acting between the electron and the positive corpuscle.

INTRODUCTION

All substances with which we are familiar have been resolved into one or more of ninety-odd elementary or atomic species. Each of these atomic species is supposedly composed of two kinds of electricity, negative electrons and positive hydrions, put together in various amounts and in various ways. These electrons and hydrions are the bricks, then, of which the universe of matter is built, and the electrical forces of attraction and repulsion acting between them are the plaster and cement, the joists and beams, which hold them together, and give to the superstructures their characteristic permanence and rigidity.

But chemical substances are neither wholly permanent nor wholly rigid, for in every chemical change we see the atom-units shifted from one molecule to another. So readily do these shiftings of atoms from molecule to molecule take place, and so great is the possible number of combinations, that the variety of possible molecular species is almost incomprehensible. Nevertheless, these unending ramifications of chemical change are rendered intelligible and subject to simple systematization through the application of the two laws fundamental to the atomic theory; the laws of definite and multiple proportion. These laws, encompassed as they are in the generalization of the theory of valence, correlate all changes in chemical composition,

and show us how chemical structure is dependent upon a simple mechanism whereby one atom can unite with other atoms through primary valence unions in constant and integrally related proportions.

Only a small part of the changes taking place about us are chemical in nature; that is, in only a few of these changes do the substances undergo any alteration in chemical composition. In the formation of liquids from gases, of solids from liquids, in the formation of surfaces and the phenomena of capillarity, in the solvent power of one substance for another, in viscosity, elasticity, rigidity, we see changes which we call physical; changes which involve only an alteration in state, and no alteration in chemical composition. Such changes cannot, therefore, be dealt with under the theory of valence, for the shifting units are molecules, not atoms, and we have no laws of definite or multiple proportions for intermolecular combinations.

The forces which bind molecules together - the cohesive forces - must, in the final analysis, prove to be analogous to the forces which bind the atoms together in the molecule, even to the forces which cement together the electrons and hydrions in the atom, for they all have their genesis in the fundamental electric charges; and each of these forces must be accounted for on the basis of the nature of these electric charges.

Nearly all the physical properties of matter are influenced to a very great extent by chemical constitution, e. g. by the mode of

chemical combination of the atoms in the molecule. Thus, even among isomers we find one compound differing from another in behavior by 100 to 1000 per cent. One must attribute these differences in behavior to differences in the arrangement of the component atoms. But despite the fact that there is available a vast number of data pertaining to molecular behavior, we have as yet no notion of why one molecule behaves one way and another quite differently under the same conditions - no theory to guide us through a maze of seemingly unrelated facts.

It is evident that we lack in our atomic models a mechanism which can account for the physical properties of the various molecular species with which these atoms can be built. It would be dangerous, and probably futile, to postulate such a mechanism at the present stage of our knowledge of the intimate behavior of the electric charges; we must instead attempt to correlate the physical properties, intent upon reducing them ultimately to an atomistic basis.

This, then, is our problem: the problem of comparative molecular behavior. And as we turn to primary valence and to the subatomic forces for an explanation of atomic combinations and atomic behavior, so we must look to the intermolecular forces - to secondary valence - for an explanation of molecular combinations and molecular behavior.

Chapter I.

THE CONCEPT OF SECONDARY VALENCE

By secondary valence is meant that force which binds molecules together. Secondary valence is the chemist's name for the force which the physicists call cohesion. Apart from specific cohesion, we know very little about the intimate nature of this force; so little, in fact, that it cannot be said at the present time what part of the atom (or the molecule) is responsible for molecular aggregation.

Physicists who treat the problem of cohesion usually assume that the attraction of one molecule for another is to be attributed to "stray electric fields" surrounding the valence electrons of the atom; they further assume that molecular configuration plays an important part in determining the attraction between two molecules, and that the force acting between two molecules is subject to treatment on the basis of the inverse square, or the inverse fourth power, or some such mathematical function of the distance supposedly separating them. It is within the province of this paper to show that all three of these assumptions are erroneous. Evidence derived from a study of organic compounds will be presented to show that the forces acting between molecules are comparable to those forces in the atom which are responsible for atomic structure, in that they are rhythmic in nature and are consequently not subject to treatment under familiar electro-magnetic laws.

The Principle of Constitutive Nature.

Something of the general nature of secondary valence can be deduced from familiar facts. Since all substances may exist in the liquid or solid state, all atomic species must possess some secondary valence. The characteristic intensity of secondary valence associated with any molecular species, however, depends to a great extent upon the arrangement of the atoms in the molecule. This sensitivity to constitutive* relations concerns, from a causative point of view, only one or two atoms in the entire molecule. In other words, these variations in molecular activity are attributable solely to variations in the activity of one or two atoms, and they are the result of differences in the mode of chemical combination of these atoms. There are only a few atoms which are capable of varying in their activity in this manner. We shall be concerned in the present study only with oxygen and nitrogen, the two which are undoubtedly the most important.

Consider, for example, the compounds valeric acid and water. There certainly is no reason for believing that the molecules of these substances are held together by forces of a dissimilar nature; yet when we come to combine valeric acid with water, some writers go so far as to assume that an entirely new force enters into the intermolecular

* The term constitutive should be carefully distinguished from configurative. When atoms are connected by primary valence to make a molecule, certain undefined interactions take place between them which alter their intrinsic nature. Such changes are called constitutive, since they have to do with chemical constitution. The configuration of the molecule is a hypothetical feature with which the physical chemist will rarely have to deal.

relations. Others are satisfied to proceed upon the basis that the valeric acid is not combined with the water at all, but that it is in an analogous state to a gas and occupying mythical intermolecular spaces for which there is no experimental justification. Apart from the results of this research, it seems a self evident deduction that the valeric acid molecules have much the same relation to the solvent as do other molecules of water, and that the same forces are at work between them in identically the same manner.

Yet when we compare the solubility of valeric acid with that of pentane, we see that the introduction of two oxygen atoms has worked a great change in the properties of the latter, for while valeric acid is very soluble in water, pentane is almost insoluble. If now we pass to ethyl valerate, the solubility falls off again to a vanishingly small value. Here then is the problem of constitutive behavior: Two oxygen atoms in the carboxyl group can endow the pentane molecule with properties which render it very soluble in water; but the same oxygens in the ester are essentially as inert as the carbon and hydrogen themselves.

Under any concept of secondary valence it must be admitted that the activity of one atom may vary through such wide extremes that this atom can practically determine the molecular behavior.

We have then, in resumé, a force possessed in some measure by all atoms. It may be possessed, however, by certain atoms under particular conditions in great excess. In such atoms of variable activity, it is

clear that the activity depends upon the mode of chemical combination. This is the force which we are now calling secondary valence.

The Concept of Molecular Volume.

Before we can make any progress in the analysis of the nature of secondary valence, we must introduce into all physical-chemical considerations another factor, namely, molecular volume. When a number of molecules come to positions of equilibrium with regard to electrical forces acting between them, there are obviously two factors brought into play. The first is the respective intensities of the attractions between them; the second is the relative amount of space which they occupy, or their respective molecular volumes.

Molecular volume has received little or no attention in the consideration of intermolecular relations. A study of various physical phenomena has convinced me that molecular volume is a determining factor in practically all the phenomena associated with liquids. By its use we have a means of correlating molecular behavior, and many relations are disclosed which otherwise would go unrecognized.

By molecular volume is meant the volume in cubic centimeters of a gram molecule of a particular substance, determined for certain practical reasons at the normal boiling point. Molecular volumes are additive in nature. That is, values may be obtained through the

comparison of a series of compounds for each component atom and these atomic values may then be added together to derive the molecular volume of any desired molecular species. Constitutive variations are very much in evidence, for the volumes of some atoms, especially oxygen and nitrogen, vary by nearly 100 per cent, according to the nature of their chemical union. But these constitutive influences are relatively few and constant and the results obtained justify the assumption that LeBas' methods of calculation are fundamentally sound.

The Principle of Three Dimensional Symmetry.

We have in some measure been misled by the graphical formulas which we draw upon the blackboard into believing the molecules always have rigid and characteristic configurations. It is almost second nature to think of benzene as being ring-like and of hexane as being chain-like. Such a notion is immediately dispelled by a cursory inspection of molecular volume relations. The very application of the additive principle necessitates the immediate recognition of the fact that every molecule, no matter what its chemical nature, occupies a domain which is the perfect sum (admitting constitutive relations, which of course have to do with internal and not external matters) of the space occupied by the component atoms. This means that there is neither a "hole" inside benzene, nor any "cracks" nor crevices" in hexane, as there would surely be were either of them composed of rigid spheres of carbon

with smaller rigid spheres of hydrogen tacked on at various places. The principle of the perfect sum implies that the six carbons and their attendant hydrogens make up a new domain which has the same shape as has each of the components, much as though we had put several little spheres together to make one big sphere. This rather surprising condition is initially a consequence, as I have said of the additive nature of molecular volumes, but it is substantiated in an overwhelming manner by the role of molecular volume in the phenomena of molecular physics, where there is never any indication that any molecule has any other shape than that of a sphere. That the shape of the molecular domain is not a perfect sphere in the literal sense is obvious from the same argument; for in that case there would be crevices between adjoining domains for which no allowance is made in the calculation of molecular volumes. We must rather look upon this shape as constantly varying between that of a tetrahedron and that of a sphere because of the constant agitation and collisions to which molecules of liquids are subjected. For the purposes of definition it should suffice to call it polyhedral, with the reservation that there can be no "dead" interstices between adjoining domains.

It is difficult to conceive of any atomic theory so mercurial as to explain satisfactorily the facts disclosed by a study of molecular volumes.

The atom is supposed to be a very porous affair, about as porous as the solar system. All physical experience shows us, however, that the space between the particles of electricity which compose the atom is so filled or constrained by lines of force that no two atoms can occupy the same space at the same time, or even overlap beyond certain assumed limits. Atoms thus held together by electrical forces constitute the molecule in which the atomic arrangement accounts for the chemical identity, which is never lost. We have just seen that the space relations of molecules are vastly different from what we would expect from the permanence of this atomic arrangement. The molecular volume at the boiling point is about three times what it is at absolute zero. This increase in volume is sometimes attributed to increased molecular motion. The validity of this assumption is open to question, but even if we do assume that any part of the molecular volume in the liquid state (which, for the purposes of this paper is synonymous with molecular domain) is due to molecular motion, this fraction must be statistically identical under like conditions for various molecular species. It thus becomes a universal factor which may be omitted from immediate consideration. To all intents and purposes the molecular domain is completely filled by the molecule. The boundary of the domain is purely an imaginary surface within which no other molecule can trangress. As to what the actual dimensions of the molecule may

be, and as to the proportions of this actual volume and the volume of the apparent domain, we need not be concerned at the present time. The essential idea to be gained from an analysis of molecular volume relations is that every molecule behaves as though it completely fills a definite space which has three dimensional symmetry.

Secondary valence, as has been said, is the force which binds molecules together. We must picture this union as being quite labile, for above the melting point there must be considerable molecular motion, crudely analogous to the motion of shot in a well-filled bucket which is being vigorously agitated.* As a statistical result of this motion and in keeping with the foregoing concept of molecular domains, we are entitled to think of secondary valence as acting as though it were either uniformly distributed over the surface of the molecular domain, or localized at its center. When molecular motion is restricted, as it must be at the interfaces of liquids, the molecule behaves as though its secondary valence were localized at one or more points. (It is noteworthy that here molecular volume relations fail, and the molecular assumes a definite configuration or shape). But there is no evidence to indicate that such a localization ever takes place when the molecule

* Some molecular motion in liquids is a necessary assumption to account for vapor tension, solute diffusion and the absence of a structure. But a satisfactory explanation of all these could be based, it seems, just as well upon rotational motion as upon translational motion. If this motion is assume to be largely rotational, it is evident that it would contribute but little to the molecular volume.

is completely and intimately surrounded by other molecules. In those molecules where two or more atoms actually contribute to the total secondary valence, the net result is apparently the same as though the entire secondary valence were to be attributed to one source.

Chapter II

Partition Coefficients.

The phenomena of solution, from a practical point of view, are the most important phases of molecular behavior with which the physical chemist has to deal. Solubility relations are likewise the most susceptible to constitutive influences. On this basis, no better field could be chosen for the study of the nature of the forces acting between molecules. But a study of absolute solubilities is impractical because most of the lower members of chemically homologous series are miscible with water in all proportions, and hence they are excluded from direct consideration.

The problem may be approached, however, through a study of partition coefficients; for when a solute distributes itself between two immiscible liquids the amount in each of the liquids is an index of the relative solubility of the solute in the respective liquids. By determining the partition coefficients of a large number of compounds between any two immiscible liquids, such as water and xylene, it is possible to obtain an idea of the nature of the electrical forces involved in solution. When an aqueous solution of any substance is shaken with an immiscible liquid, some of the solute will pass from the water to the other liquid. The ratio of the concentration of the solute in the second liquid to the concentration in the water, after equilibrium has been attained, is called the distribution of partition coefficient. Under ideal conditions the amount of solute passing into

the second liquid would be proportionate to the concentration in the water, and the partition coefficient would be constant and independent of the total concentration; that is, we might write $C_2/C_1 = k$. This simple state of affairs is rarely met with, however, for practically all the substances with which we are concerned are dissociated in water, and many of them are associated in organic solvents. Since electrolytic ions do not exist in a dissociation solvent, such as xylene, and since associated molecules do not exist at great dilution in a dissociating solvent, such as water, both the dissociated and associated fractions of the solute in the two respective layers are removed from the system, so to speak, for neither can pass as such to the other layer. Hence, at a given total concentration, dissociation tends to lower the partition coefficient and association to raise it.

Any attempt to compare the partition coefficients of various substances would obviously be futile until both of these disturbing factors have been eliminated. Dissociation, which proceeds according to well-known laws, can be corrected for on the assumption that the concentration in the second phase is proportionate to the undissociated fraction in the water. From the dissociation constant we can calculate the percentage dissociation at a dilution equivalent to the concentration in the water when equilibrium has been reached, and the partition coefficient then becomes: $C_2/C_1 (1-a) = k$. But there are only a few instances where this correction for dissociation suffices to hold the

partition ratio constant over a large range of total concentrations, for most compounds, especially among the organic acids, are associated in organic solvents.

The mechanism involved in this association is comparable to that of dissociation, if we but think of the associated molecules in the organic solvent as similar to the undissociated molecules in water, and the single molecules in the organic solvent as similar to electrolytic ions. In concentrated solutions a larger fraction of the solute will be associated than in dilute solutions, and for intermediate concentrations all progressive degrees of decomposition of the associated fractions will be possible. But the analogy is imperfect, in that the maximum degree of association is unlimited; that is, the solute may be associated into aggregations of two, three, four, etc., molecules. Such aggregations as exist, however, would be expected to decompose at a rate constant and characteristic for each molecular species, comparable in a sense to the rate at which the single molecules decompose into electrolytic ions in water. This "decomposition constant" might be determined by studying both concentrated and dilute solutions, but there are reasons to believe that even this would not suffice to untangle the web. Water will dissolve in the second solvent, and thus upset the association constant, and the second solvent will dissolve in the water, and upset the dissociation constant. Furthermore, in some cases the partition coefficient increases with decreasing total concentration. This cannot be accounted

for on the basis of either association in the second liquid, or dissociation in the water. It may be due to hydration. So complex do these disturbing factors become that it seems almost futile to attempt to correct for them on a stoichiometric basis. For our purposes it is necessary to have values which represent the true tendency of the various species to pass from the water to the other solvent and any variations introduced by these disturbing factors would materially affect the interpretations to be placed upon them. We have no way of knowing whether we have eliminated the disturbing factors or not, except as we anticipate in some measure the results which we may reasonably hope to obtain.

Before beginning a search for a suitable method of correction several conditions were set down which any correction, to be satisfactory, would be expected to meet. If we compare the partition coefficients of a series of allied compounds, determined at the same total concentrations, into two solvents, such as chloroform and xylene, we see that the partition coefficients into the one solvent bear approximately a constant ratio to the partition coefficients into the other. This ratio is maintained fairly well so long as the compounds investigated have a similar dissociation constant; but when we include a compound which departs from the average in this respect, the ratio is materially altered. It seems a reasonable assumption that, if properly corrected for dissociation and association (if this latter occurs), this ratio would prove to be a constant. If we designate the properly corrected partition coefficient by P, we might then write

$$\frac{P \text{ Chloroform}}{P \text{ Xylene}} = \text{Constant}$$

This simple relation should apply at least to nearly related substances, if we may judge from our experience with uncorrected partition coefficients. Furthermore, the ratio between the partition coefficients of any two compounds should be maintained regardless of the concentration at which the partition coefficients are determined, the nature of the solutes, and the nature of the second solvent. Since we are looking for certain relations among homologous compounds, we may in fairness anticipate them and require that our method of correction yield results which are subject to a reasonable interpretation. It would follow from the previous conditions that this interpretation would be essentially independent of the nature of the second solvent.

It would hardly be worth while to fill up several pages with test cases showing how methods of correction based upon dissociation constants and association factors fail in one or more respects to fulfill the above requirements. It is more to the point to discuss briefly the only method I have found so far which does appear to be satisfactory. It is unfortunately empirical and it cannot be said to be founded upon any physical-chemical experience whatsoever. The sole excuse for its use lies in the results obtained by it, and on these results alone can one base an opinion as to its validity.

The Method of Correction.

We will consider the corrected partition coefficient, P, to be the ratio of the concentration in the second solvent to the concentration in the water (C_2/C_1) when the concentration in the second solvent has some arbitrary and unitary value. That is, P = C_2/C_1 when C_2 is 100 millimols, 10 millimols, 1 millimol, etc., per liter. This is similar to the method first advocated by Nernst; i. e., deriving a constant ratio through the use of an exponential equation: $\frac{C_2}{C_1^{\,y}} = k$, where y is an uncharacterized exponent. The method differs from Nerst's in that no mathematical manipulation is involved, for in no case is y constant over a large range of total concentrations, and consequently the equation can never be ideally fulfilled, but we can determine the partition coefficient at suitable total concentrations so that we will actually pass, or approach very close to, a given concentration in the second solvent, and we thus reduce the possibility of introducing error through interpolation to a minimum.

A few case have been cited from the literature to illustrate the application of this method of correction. If we compare the partition coefficients of several substances between water and several solvents, all of which solvents are relatively insoluble in water, we find that the ratio between the partition coefficients into one solvent and the partition coefficient into another solvent is a constant, and that it is independent of the concentration chosen for C_2.

The data upon which the following interpolations have been based are given in full in Section I of the tables given in the experimental part of this paper. Below I have given only the concentration in the second solvent to which interpolation is made, the corrected partition coefficients, and the ratios between these partition coefficients.

Table I

	C_2 (m/L)	P CCl_4	P Toluene	P Tol. / P CCl_4	P Benzene	P Benzen / P Toluen
etic acid	1000.0	0.10	0.12	1.20	-	-
loroacetic acid	1000.0	0.06	0.07	1.17	-	-
enol	1000.0	2.45	2.75?	1.12	4.3	1.56?
imethylamine	1000.0	-	0.43	-	0.50	1.16
ridine	100.0	-	2.06	-	2.60	1.34
loroacetic acid	100.0	-	0.028	-	0.036	1.30
tyric acid	1.0	0.115	0.16	1.39	0.215	1.26

It will be noticed that here we have a weak acid, a moderately strong acid, an alcohol, a weak base, and a ketone. Some of these we know to be associated in organic solvents; most of them we know are dissociated in water; nevertheless the ratios of the partition coefficients between water and carbon tetrachloride, and water and the other solvents are fairly constant. It is quite impossible to get this result with any other method of correction, especially with those compounds which show association in the organic liquids.

If, now, one of the solvents under comparison is soluble in water, the ratios vary with the different arbitrary values for C_2 which are chosen for extrapolation. Thus, chloroform is much more soluble in water than is benzene or toluene. The ratio of the more soluble solvent over the less soluble one increases as lower values are chosen for C_2.

Table II.

	C_2 (m/L)	P $CHCl_3$	P Benzene	P $CHCl_3$ / P Benzene	P Toluene	P $CHCl_3$ / P Tol.
Acetic acid	1000.0	0.20	-	-	0.12	1.67
Phenol	1000.0	5.50	4.3	1.28	-	-
Chloroacetic acid	100.0	0.062	0.0365	1.70	0.028	2.22
Acetic acid	100.0	0.10	0.054	1.85	-	-
Butyric acid	1.0	0.385	0.215	1.79	0.18	2.40

If the two solvents are equally soluble in water, this divergence disappears, as can be seen from the comparison of chloroform and bromoform.

Table III.

	C_2 (m/L)	C $CHCl_3$	P $CHBr_3$	P $CHCl_3$ / P $CHBr_3$
Acetic acid	1000.0	0.20	0.148	1.35
Phenol	1000.0	5.50	4.30	1.28
Chloroacetic acid	1000.0	0.125	0.094	1.33
Ammonium	100.0	0.038	0.029	1.31
Picric acid	100.0	2.20	1.60	1.37

Though the evidence which has been given so far is not very comprehensive, it is sufficient to show that so long as we use the same arbitrary value for C_2 for interpolation, the partition coefficients of various species, so derived, into any one solvent are subject to comparison; for since the partition coefficient of several compounds into two or more solvents bear a constant ration to each other, all irregular influences arising in the nature of the second solvent are eliminated.

The values of the partition coefficient for any two compounds so obtained maintain a constant ratio to each other regardless of the nature of the second solvent, the total concentration, or the chemical nature of the solute. The truth of this last condition can be seen in table IV.

Table IV.

	C_2 (m/L)	P Acetic acid	P Chloroacetic acid	P Acetic acid / P Chloroacetic acid
Chloroform	1000.0	0.20	0.125	1.60
Bromoform	1000.0	0.148	0.094	1.57
Toluene	1000.0	0.12	0.07	1.71
Carbon tetrachloride	1000.0	0.10	0.06	1.66
Chloroform	100.0	0.10	0.062	1.61
Benzene	100.0	0.054	0.0365	1.48
Chloroform	1.0	0.0725	0.0438	1.65
Xylene	1.0	0.030	0.0175	1.71

The partition coefficient is independent of the relative amounts of water and second solvent used.

Table V.

Phenylacetic acid into Xylene

	C_2	P
1 Vol. xylene to 1 vol. water	1m/L	0.510 x 1 = 0.510
1 Vol. xylene to 2 vols. water	0.5m/L	0.253 x 2 = 0.506
2 Vols. xylene to 1 vol. water	2m/L	0.02 - 2 = 0.510

We have now obtained fixed values for these partition coefficients where otherwise they would move indefinitely through a wide range because of at least five disturbing factors. The relative concentrations of any solute in the two solvents are indicative of the relative solubilities of the solute in those solvents. And since the concentration in the second solvent is always the same, the concentration in the water becomes a measure of the tendency of that solute to leave the aqueous environment and pass into the other environment, or a measure of the molecular fugacity. Further evidence will be brought out in the discussion to substantiate the method of correction, for by it are revealed many relations which have never been revealed by any other method of correction.

But it must be kept in mind that comparisons are valid only between values of P derived from the same arbitrary concentration in the second solvent (C_2). For the purposes of this paper, the optional value of C_2 chosen for interpolation is 1.0 millimol per liter, for nearly all acids and bases are sufficiently soluble in water to permit our passing this concentration experimentally. A very short inter-

polation between values for C_2 greater than 1 m/L and less than 1 m/L is all that is necessary to obtain the corrected partition coefficient P. In only a few cases (and the majority of these are cited from the literature) has this interpolation been made from values entirely above, or entirely below, this arbitrary concentration.

Experimental Methods.

Aqueous solutions of known titer were shaken for three to five minutes with equal volumes of the second solvent. The mixture during shaking was contained in either a separatory funnel or a stoppered Erlenmeyer flask. Previous to shaking, the containing flasks and the solutions were brought to 25° .5, by immersion in a water bath, and after shaking the mixture was allowed to separate in the water bath. After separation, portions of the aqueous layer were titrated, and the concentration in the second solvent was determined by difference. The volatile nature of most of the materials studied and the extent of the work involved made it impractical to determine the concentrations in the second solvent directly. All titrations were made with standard hydrochloric acid and sodium hydroxide solutions, using phenolsulphonphthalein and methyl orange.

The bases were, for the most part, from freshly opened bottles of Kahlbaums' C. P. Reagents. For these, and for some of the acids, I am indebted to Dr. Carl Voegtlin, whose co-operation in this matter has

gone far to make this work possible. I am also indebted to Dr. E. K. Marshall, Jr., for some of the bases. The remaining preparations were secured from the Eastman Kodak Company. In as much as this research was intended as a preliminary survey of the field, no attempt was made to obtain a degree of accuracy commensurate with physical research. None of the liquid chemical compounds was repurified, though practically all the crystalline compounds were recrystallized. The greatest difficulty in securing suitable checks lies in the extracting solvent. A slight contamination here of the proper sort will prove very disastrous. The xylene and chloroform were carefully repurified by shaking with strong alkali and then with five per cent sulphuric acid, and redistilling over a mixture of calcium oxide and calcium chloride. The method offers little experimental difficulty, but a few sources of systematic error were found which may be worth mentioning. Solutions of both amines and acids will decrease greatly in strength if violently shaken for a few moments, due evidently to increased surface adsorption. This adsorbed material diffuses very slowly into the solution again, and to guard against this effect, a sufficient interval of time should be allowed to elapse between sampling. The effect is especially pronounced immediately after making a solution of a liquid chemical compound, and after emulsification with an immiscible solvent. Five to ten minutes was always allowed after shaking to let the solution regain "diffuse" equilibrium. The amines, being very

volatile, are easily lost from their aqueous solutions and the water layer should not be run out of a separatory funnel before titration. Samples can be taken direct from the funnel by blowing a small bubble of air through the pipette to expel the other solvent. Phenolsulphonthalein gives a clean end-point with nearly all the amines (except the anilines of course), but it is not as satisfactory with the weaker acids. Where the partition coefficient is very small, an obscure end-point makes the determination very difficult. It is as satisfactory, however, as any other indicator for the purpose, and has the advantage that one can tell with it just what carbon dioxide is doing. By sucking through the pipette before sampling to clear out any carbon dioxide from the breath, difficulties from this source could be eliminated.

In the following tables, the first section comprises material quoted from the literature, and the second section, the original contributions. The column headings need no explanation beyond the statement that unless otherwise indicate, all concentrations are expressed in millimols per liter.

Chapter III

THE PARTITION COEFFICIENTS INTO XYLENE

In the first chapter the generalized concepts of molecular volume and secondary valence were discussed in some detail. On the assumption that molecular volume is one of the essential or determining factors in all intermolecular relations of liquids we are going to use it in the analysis of the relations involved in partition coefficients.

The choice between molecular volume and molecular weight is not one which can be settled by literal proof. In the end it is a matter of interpretation and a decision must rest upon the relative value of the results to be obtained by the use of each. The reader is urged to keep in mind that such disclosures as are made through the use of molecular volume would not appear were one considering molecular weight; in fact, there would be no intelligible relationship whatever. This is especially true when we consider compounds containing halogens, ring formations, hydroxyl groups, ethylene linkages, etc., because then the relative differences in mass and volume become very great. It is a part of the purpose of this paper to establish the role of molecular volume in the intermolecular relations under consideration; and it is held that this role is established by the fact we are rewarded for its use with a significant simplification in these relations.

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When we plot the logarithms of the partition coefficients of the amines and the acids into xylene against their respective molecular volumes we obtain the pictures reproduced in Figures 1 and

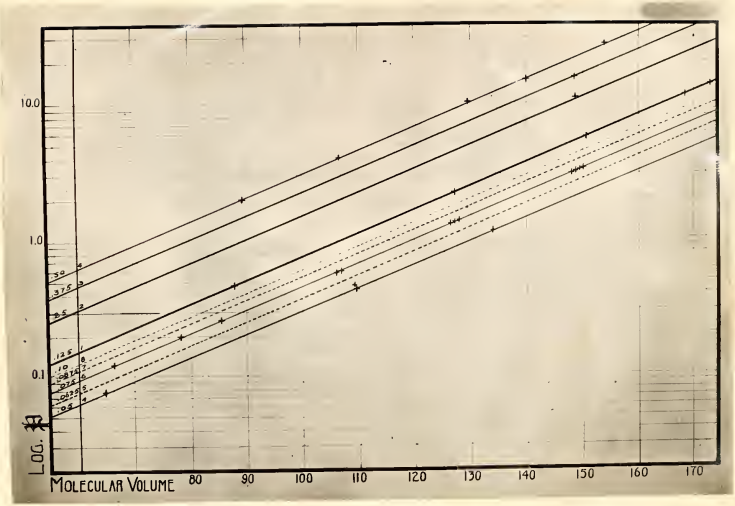

Figure I.

THE PARTITION COEFFICIENTS OF THE AMINES BETWEEN WATER AND XYLENE.

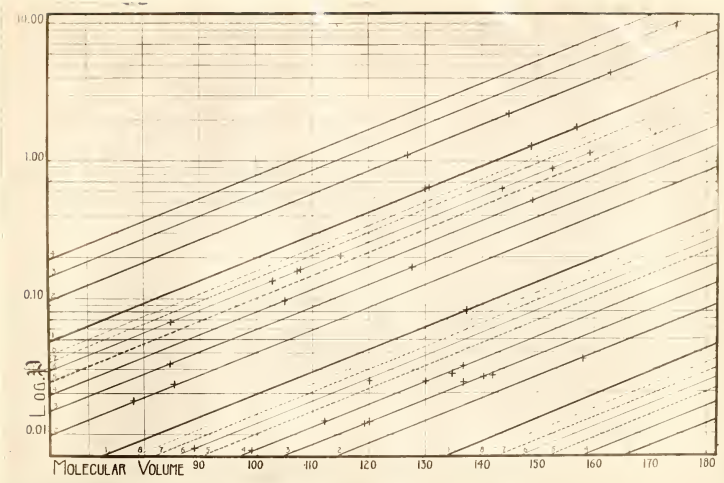

Figure II.

THE PARTITION COEFFICIENTS OF THE ACIDS BETWEEN WATER AND XYLENE.

II. Three outstanding facts are revealed by a glance at these pictures:

1. The observed points fall into several SERIES, each of which is a straight line.
2. These SERIES are all parallel.
3. The distances which separate the various SERIES are related in a definite and periodic manner.

The equation for the straight line can be applied to any one of these SERIES by extrapolating to $V_m = 0$; with the constant of integration a thus obtained, the angular constant, or constant of proportion, k can be calculated from the following equation:

$$\text{Log } 100\ P = \frac{V_m}{K} - a \qquad (1)$$

On the basis of careful extrapolations the angular constant k has been given the value 60.00. This constant is common to all SERIES since they are parallel.

The compounds which have been studied will be considered according to the SERIES in which they fall. In the following tables the second column gives the molecular volumes; the italicized figures are observed values cited from Le Bas, and the others are calculated by Le Bas' rules. In column three, the observed values of the partition coefficients, P, are given and in the fourth column the values of P as calculated from the equation given above using the SERIES constant a. The ratios of the observed and calculated values

in the fifth column are mathematical equivalents of statements 1 and 2 above.

Table I.

The Partition Coefficients of the Bases, by Series; Xylene.

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 4; a = + 0.8239				
Pyridine	89.5	1.95	2.07	106.1
Anilin	106.6	4.00	3.98	99.5
Methylanilin	129.6	10.45	9.19	114.0
Quinoline	140.0	14.0	14.36	102.4
Camphylamine	174.0	54.2	52.9	97.7
Bornylamine	174.0	54.0	52.9	97.9
SERIES 3; a = + 0.6989				
Xylidene, 1.4.3.	148.6	14.9	14.98	100.4
SERIES 2; a = + 0.5229				
Xylidene, 1.3.4.	148.6	11.0	10.00	90.8
SERIES 1; a = + 0.2218				
Trimethylamine	88.0	0.47	0.488	103.9
Benzylmethylamine	151.0	5.1	5.49	107.5
Heptylamine	169.5	11.2	11.14	99.6
Benzylethylamine	173.0	13.4	12.74	95.2
SERIES 8; a = +0.1249				
SERIES 7; a = + 0.06695				
SERIES 6; a = +0.0000				
Methylamine	43.0	0.051	0.052	102.0
Dimethylamine	66.3	0.125	0.127	101.8
Allylamine	78.5	0.198	0.203	102.5
Propylamine	85.7	0.26	0.268	103.0
iso-Butylamine	106.3	0.58	0.591	101.9
n-Butylamine	106.8	0.60	0.602	100.1
iso-Amylamine	127.0	1.38	1.310	95.0
Benzylamine	127.4	1.40	1.328	94.9
n-Amylamine	127.5	(1.46)	1.340	(91.7)
n-Hexylamine	148.0	3.05	2.925	96.0
Dipropylamine *	(148.0?	3.15	(2.925	(92.7)
	) 151.5		3.347	107.2
Triethylamine *	148.0?	3.17	(2.925)	(92.2)
	152.6		3.494	110.0

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 5; a = -0.0792				
SERIES 4; a = -0.1761				
Ethylamine	64.6	0.077	0.0798	103.5
Piperidine	108.8	0.44	0.434	98.6
Diethylamine	109.3	0.44	0.442	100.2
Methylpiperidine	133.8	1.20	1.132	94.5
Coniine	175.6	6.0	5.63	94.0
			Average	100.8

* Both dipropylamine and triethylamine behave as though they had a volume nearly equivalent to hexylamine; secondary and tertiary nitrogen has a larger volume than primary nitrogen, and the low observed values may be due to impurities.

Table II.

The Partition Coefficients of the Acids, by SERIES; Xylene.

SERIES 4; a = + 0.2354				
SERIES 3; a = + 0.1100				
iso-Amylacetic acid	174.1	10.7	10.40	97.3
Heptoic acid	174.6	10.0	10.48	104.8
SERIES 2; a = -0.0655				
Benzoic acid	126.9	1.10	1.12	101.8
Cinnamic acid	162.7	4.5	4.43	98.5
SERIES 1; a = -0.3666				
Valeric acid	130.0	0.635	0.631	99.5
Salicylic acid	130.6	0.650	0.646	99.5
Piperonylic acid	148.7	1.29	1.29	100.0
Anisic acid	156.5	1.80	1.75	97.2
Hydrocinnamic acid	170.1	2.75	2.94	106.9
SERIES 8; a = -0.4634				

	Vm	P obs.	P calc.	P obs. / P calc.
SERIES 7; a = -0.5214				
SERIES 6; a = -0.5884				
Formic acid	41.5	(0.0125)[1]	0.0125	100.0
Acetic acid	64.0	(0.030)[1]	0.030	100.0
Propionic acid	85.3	0.066	0.068	103.0
α-Crotonic acid	102.1	0.135	0.130	96.3
sec.-Butyric acid	107.3	0.160	0.158	98.8
n-Butyric acid	107.8	0.158	0.161	102.0
β-Iodopropionic acid	115.0	0.208	0.213	102.5
iso-Valeric acid	129.5	0.370	0.371	100.2
o-Chlorobenzoic acid	143.3	0.635	0.631	99.4
p-Nitrobenzoic acid	152.5	0.900	0.898	99.8
o-Iodobenzoic acid	159.4	1.15	1.17	101.8
SERIES 5; a = -0.6676				
m-Nitrobenzoic acid	151.9	0.73	0.731	100.1
SERIES 4; a = -0.7645				
β-Bromopropionic acid	105.8	0.095	0.099	104.2
Phenylacetic acid	148.9	0.51	0.521	102.2
SERIES 3; a = -0.8894				
Bromoacetic acid	84.5	0.033	0.0333	100.0
α,β-Dibromopropionic acid	127.8	0.168	0.174	103.5
SERIES 2; a = -1.0655				
Acetic acid	64.0	(0.010)[2]	0.10	100.0
Chloroacetic acid	78.0	(0.0175)[1]	0.0172	98.3
Pyruvic acid	85.3	0.0235	0.0227	96.6
3.5-Dinitrobenzoic acid	175.8	0.70	0.732	104.5
SERIES 1; a = -1.3665				
SERIES 8; a = -1.4634				
SERIES 7; a = -1.5214				
SERIES 6; a = -1.5884				
Lactic acid	88.7	(0.00792)[3]	0.00774	97.7
o-Nitrobenzoic acid	150.8	0.085	0.0841	99.9
SERIES 5; a = -1.6676				

	Vm	P obs.	P calc.	P obs. / P calc.
SERIES 4; a = -1.7645				
Oxalic acid	75.6	$(0.003)^4$	0.0031	(103.3)
Malonic acid	97.8	$(0.0077)^4$	0.0073	(94.8)
Laevulinic acid	130.0	0.0242	0.0262	108.2
Itaconic acid	134.3	$(0.0286)^4$	0.0298	(104.2)
Resorcinilic acid	136.4	0.032	0.0324	102.2
Acetylsalicylic acid	185.6	0.222	0.2132	96.0
SERIES 3; a = -1.8894				
Succinic acid	120.0	$(0.0123)^4$	0.0129	(104.8)
Centisinic acid	136.5	0.0242	0.0243	100.3
Bromosuccinic acid	140.5	0.0252	0.0283	112.3
Glutaric acid	142.2	$(0.0253)^4$	0.0302	(119.2)
2.4-Dinitrobenzoic acid	175.3	0.1003	0.1077	107.7
Pimelic acid	186.6	$(0.139)^4$	0.166	(119.2)
Suberic acid	208.8	$(0.345)^4$	0.389 .	(112.8)
Azalleic acid	231.0	$(0.95)^4$	0.913	(95.1)
SERIES 2; a = -2.0655				
Maleic acid	112.6	$(0.00668)^4$	0.00647	(96.8)
o-Phthalic acid	155.6	0.0355	0.0337	95.0
Benzilic acid	283.3	0.800	0.805	99.3
SERIES 1; a = -2.3665				
- - - - - - - - - -				
SERIES 3; a = -2.8894				
Camphoric acid	215.7	0.048	0.051	106.2
			Average	101.4

NOTE: In many instances the partition coefficient between water and xylene is too low to be determined directly. It is possible to calculate this partition coefficient if the probable ratio between P xylene and P for another solvent is known. This calculation gives only one of several possible values for P xylene, and therefore figures so obtained cannot be used in making comparisons of the constitutive behavior of several compounds. But the fact that the values so obtained agree with the SERIES behavior is important, and so in order to show this agreement and to complete the chemical groups in the above table, a few such calculated values have been included. For the derivation of the following ratios see

1. - Calculated from chloroform, ratio 2.5 to 1, p. 2, sec. II.
2. - Calculated from toluene, ratio 1 to 1. Cf. H. and F. p. 2, sec. I. Also from chloroform, ratio 2.5 to 1. Cf. D. and G., (20°), p. 2, se
3. - Calculated from chloroform, ratio 2.5 to 1.
4. - Calculated from ether, ratio 10 to 1. Cf. Chandler, p 2. sec. I.

The Role of Molecular Volume

The above tables through the application of Equation I establish the fact that all these SERIES are straight lines and parallel. The function of molecular volume may be briefly stated as follows:

> In any SERIES, the partition coefficient is a simple logarithmic function of the molecular volume.

That is, for any change in molecular volume, there is a corresponding change on a percentage basis in the partition coefficient. Since the angular constant is the same for both the amines and acids, the function of molecular volume is the same in both cases.

The Distances between SERIES

The most interesting aspect of these pictures is the distance which separates the various SERIES. This distance is actually given by the respective values of a, as given in Tables I and II; but these values are logarithmic and their real significance is not evident until they are converted into their corresponding arithmetric values, or antilogs. Moreover, the values which have been given for a, and which are used in Equation I, are related to the particular ordinate $V_m = 0$, and would be numerically different were another volume chosen for comparison. So the universal relationship between the SERIES, applying to any volume whatever, may be more easily understood if described in this manner.

> The SERIES delimit arithmetrically related INTERVALS or increases in the partition coefficients. These INTERVALS fall naturally into OCTAVES, each OCTAVE containing eight INTERVALS. Each OCTAVE comprises an increase of 10 times in the value of the partition coefficient. In terms of P, the first seven INTERVALS are arithmetrically equal; the eighth and last INTERVAL in any OCTAVE is arithmetrically twice the value of each of the preceding seven.

Since all experimental values fall upon one or the other of these SERIES, the possible partition coefficients at any given volume are related to each other by definite multiples of a common factor P, which is given numerically in the value, in terms of P, of the first SERIES of any OCTAVE at that volume.

Suppose we choose in Figure I the ordinate: $V_m = 54.2$; then on this ordinate the possible partition coefficients are as follows:

	Possible partition coefficients.	Series number.
	1.25	1
	2.50	2
	3.75	3
First	5.00	4
OCTAVE	6.25	5
	7.50	6
	8.75	7
	10.00	8
	12.50	10
Second	(25.00)	(20)
OCTAVE	(37.50)	(30)

(This arrangement has been illustrated at the left-hand margin of Figure I).

The OCTAVES

Thus in passing up a particular ordinate from P = 1.0 to P = 10, we cross nine SERIES or eight INTERVALS. The value of the ninth SERIES, instead of being nine times 1.0, is ten times 1.0, thus beginning another OCTAVE. This ninth series completes a group of eight INTERVALS, seven of which are arithmetrically equal, each having a value of 1.0. The eighth INTERVAL has a value of 2.0, or twice the value of any INTERVAL in the preceding seven. A little consideration will show that this peculiar arrangement is nothing more than a consequence of dividing an increase of ten times in the value of P into eight parts, when P progresses logarithmically. This may perhaps be better understood if we think of one OCTAVE as represent- the total change which may take place in the molecule under given circumstances, and further suppose that the essential condition to be fulfilled is that an OCTAVE must end at ten times the value of P at which it began.

The SERIES Numbers

From what has been said, it can be seen that, at any volume, the possible partition coefficients are related to each other as multiples of a common factor, and that the decimal value of the highest common factor depends simply upon the decimal value of P under consideration. Now since the multiple number of any SERIES, or its relative position in the OCTAVE, is always the same, the

relative position of a particular series in any OCTAVE may be indicated by its multiple number; thus the NUMBER of any SERIES refers to its position in the OCTAVE, but since all of the octaves are identical in respect to the inter-relations of the comprised SERIES, any SERIES may be considered irrespective of the particular OCTAVE in which it falls. In other words, SERIES 6 in one OCTAVE is comparable to SERIES 6 in any other OCTAVE.

The Importance of the SERIES Numbers.

From the preceding paragraph it can be seen that each SERIES possesses a characteristic individuality, so to speak, because of its position in the OCTAVE. That this characterization is of fundamental importance is borne out by a consideration of the constitutive relations disclosed in Tables I and II.

Considering first Table I, we see that pyridine, aniline, methylaniline, quinoline, and collidin fall in SERIES 4; benzylmethylamine and benzylethylamine in SERIES 1, the majority of the aliphatic amines in SERIES 6, and the piperidine derivatives in SERIES 4. No general rules for constitutive behavior can be laid down, for there are obvious exceptions to the principle of chemically homologous groups, but despite the exceptions, one cannot but feel that chemical constitution is a very important factor in determining the SERIES behavior.

Turning to Table II, we see that the aliphatic acids, up to and including iso-valeric, fall in SERIES 6 (cf. aliphatic amines, also SERIES

6). Valeric acid slips from SERIES 6 to SERIES 1, and heptoic acid to SERIES 3. Caproic acid should presumably fall in SERIES 2.* The majority of the dibasic acids fall in SERIES 3. These are only a few of the many instances which might be discussed in connection with constitutive behavior, but they are sufficient to show that

> The number of the SERIES in which a compound falls is indicative of some fundamental property of that particular molecular species under the given conditions.

The Blank SERIES

If we summarize the distribution of compounds by SERIES, we see that the vast majority of them fall in SERIES 1, 2, 3, 4 and 6. (In the following table, the partition coefficients of the amines and acids between water and chloroform have been included. These partition coefficients will be considered in detail in the latter part of this paper.

SERIES number	No. of observed cases
1	19
2	17
3	23
4	22
5	(1) ?
6	35
7	None
8	(1) ?

* See footnote, page 37

This uneven distribution in the OCTAVE is emphasized by the behavior of chemically related compounds. Attention has already been called to the behavior of valeric acid, which left the company of formic, acetic, propionic, butyric and iso-valeric acid in SERIES 6 to go into SERIES 1. It might have gone into SERIES 7 or 8, but it didn't. Again in the amines, benzylamine appears in SERIES 6, with the aliphatic amines, while benzylmethylamine and benzylethylamine avoid SERIES 7 and 8 to appear in SERIES 1. There are numerous other instances which might be mentioned to show that when a compound deviates from the behavior of allied compounds, it carefully avoids these blank SERIES.

The fact that there are so very few instances of compounds falling in SERIES 5, 7 and 8, suggests that the three which have been so far observed may be regarded as anomalies.* But since there is no

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* The exceptions to this distribution in SERIES 1, 2, 3, 4 and 6 are:

	SERIES No.	P obs.	P calc.
m-Nitrobenzoic acid (xylene)	5	0.73	0.73
n-Caproic acid (chloroform)	8	6.10	5.99
n-Caproic acid (xylene)	?	2.37	?
iso-Caproic acid (xylene)	?	1.75	?

m-Nitrobenzoic acid properly appears in SERIES 2 in chloroform and iso-caproic acid in SERIES 6; the former was repeatedly recrystallized and there can be no question of error in the partition coefficients for the sample investigated. The caproic acids fall between SERIES 1 and 2 in xylene; it is interesting to note that their relative values are the same in both solvents:

xylene	$\frac{\text{Caproic acid } 2.37}{\text{iso-Caproic acid } 1.75}$	1.35
Chloroform	$\frac{\text{Caproic acid } 6.1}{\text{iso-Caproic acid } 4.6}$	1.32

It was impossible to redistill either of the small samples of these compounds available, but it is hoped that new samples will correct this anamolous behavior.

apparent reason why compounds should not fall in these SERIES the time has not yet come to worry about them. The fact remains that SERIES 5, 7 and 8 appear to represent impossible - or very improbable conditions, and this peculiar distribution in the OCTAVE may turn out to be significant in the final consideration of the underlying mechanism.

Some General Considerations.

Secondary valence has already been defined as the force which binds molecules together. As a first step in the simplification of our problem, it was assumed that there is only one force involved in this union. It was pointed out that under this supposition it was necessary to further assume that this force depended to a very great extent upon the chemical constitution of the molecule.

The partition coefficient is an index of the relative solubility of a substance in the two solvents, and consequently it is an index of the extent of the forces involved in the process of solution. We have just seen that the partition coefficient depends upon two factors: one is molecular volume; the second factor, made evident in the rhythmic variation in the partition coefficient, can only be construed to indicate abrupt changes in the intensity of secondary valence characterizing the various molecular species. Since the role of molecular volume is identical in all cases, it is obligatory to assume that those compounds falling in a particular SERIES have a

common intrinsic intensity of secondary valence. This deduction is supported by the constitutive relations previously discussed; for if chemical constitution has anything to do with the intensity of secondary valence, we would certainly expect chemically homologous groups, such as the anilins, the aliphatic amines, the piperidines and the aliphatic acids to behave in a similar fashion.

If, then, compounds falling in the same SERIES are alike in regards to secondary valence, the separation of the various SERIES by definite distances must mean that

> the characteristic intensity of secondary valence in various molecular species differs by definite and related amounts.

In Part 1 it was shown how the intensity of secondary valence associated with any molecular species depended upon the arrangement of the atoms in the molecule. These constitutive relations concern - and this is extremely important - only one or two atoms in the entire molecule. Yet these one or two atoms can endow the molecule with its characteristic secondary valence and thereby determine the molecular behavior. Such atoms (of which oxygen and nitrogen are the most important) may themselves vary in activity between wide extremes. Any variations relating to comparative molecular behavior must be attributed to changes in these particular atoms. (In the amines, it is obviously the nitrogen which is concerned; in the acids, it is principally the hydroxylic oxygen). Now this

rhythmic variation in secondary valence is displayed by all types of compounds derived from amino nitrogen and acidic oxygen; the value of the unit increase is the same in every case, and the peculiar distribution in the OCTAVE (i. e. in SERIES 1, 2, 3, 4 and 6) likewise relates to all the compounds so far studied. These facts lead us to an extremely important deduction, namely:

> Secondary valence must be attributed to some part of the atom which is common to, and identical in its nature, in all atomic species.

The great susceptability of secondary valence to constitutive relations and the fact that in some atoms it varies between wide extremes shows us that

> this atomic mechanism may vary in different atoms in its ability to make itself felt. It functions, so to speak, in a rhythmic fashion, and its activity is determined by the mode of chemical combination.

Since all atomic species may exist in the liquid state,

> all atomic species must possess some secondary valence.

It is not possible to state any relation between this minimum, or basal elementary value, and the value which a given species will have when combined with other atoms in the molecule; so it may be necessary to consider ultimately both a basal elementary value and a basal atomic value in the state of chemical combination with other elements. In any event, it is evident that the fluctuations which we have been observing are in addition to this basal atomic value. Now the question arises,

what are the limits to the fluctuations in secondary valence associated with any one atom? Examination of the available data shows that compounds containing only one atom characterized by variable activity, such as oxygen and nitrogen, are always encompassed within one OCTAVE. It is only when two such atoms are present in the molecule, as in the hydroxyl acids, the dicarboxylic acids, etc., that the compounds is found in the second OCTAVE, or more than eight intervals removed from any compound containing but one variable atom. This fact, together with the repetitive and self-contained nature of the OCTAVE and its exact arithmetric equivalence to an increase in the partition coefficient of ten times, leads to the supposition that

> one atom may furnish, in addition to its basal atomic value, one OCTAVE, or eight units of secondary valence. Two atoms may furnish presumably as many as sixteen, though constitutive interactions usually reduce the net amount.

It does not follow that any atom will vary in this manner; carbon and hydrogen appear to possess a constant and low value.

If all the molecules under consideration contained only one variable atom, these molecules would all fall within the limits of one OCTAVE. But many compounds have been included in this study which contain several such atoms; hence these compounds are found scattered through two and even three OCTAVES. Each successive OCTAVE must be looked upon as complete, though possibly adjoining other OCTAVES by virtue of the superimposition of the last SERIES of one with the first SERIES of the other.

Chapter IV.

THE PARTITION COEFFICIENTS INTO CHLOROFORM

The partition coefficients of the acids and amines into chloroform have been analyzed in the same manner as were those into xylene. A comparison of Figure III with Figures I and II will show that the gross relations are identical. The angular constant, k, is the same in all cases, i. e. 60.00, and hence the chloroform SERIES are parallel to the xylene SERIES. The inter-relations of SERIES are the same as far as general proportionality is concerned, though the absolute values of a differ; in chloroform, P for a particular SERIES at a given volume has just five times the value that it has in xylene.

In Tables III and IV the partition coefficients into chloroform have been tabulated just as were the partition coefficients into xylene. The calculated values given in these tables are derived through Equation I, using the SERIES constants a as indicated, and the universal constant k = 60.00. The agreement between the observed and calculated values shows that the chloroform series constitute straight and parallel lines; since the SERIES constants are based upon the ideal existence of OCTAVES with related SERIES as found in the case of xylene, it can readily be seen that there is no essential difference in the fundamental relationships in xylene and chloroform. The distribution of compounds by SERIES has already been given in the previous section.

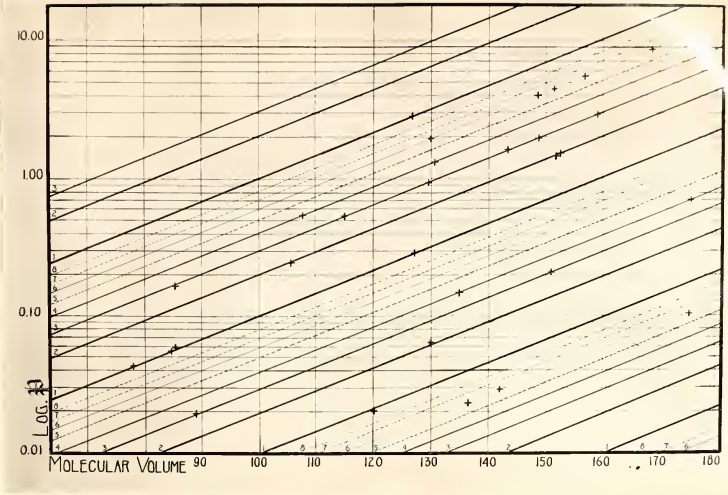

Figure III.

THE PARTITION COEFFICIENTS OF THE ACIDS BETWEEN WATER AND CHLOROFORM.

Table III.

The Partition Coefficients of the Bases, by SERIES; Chloroform.

	Vm	P obs.	P calc.	P obs. / P calc.
SERIES 2; a = + 0.2219				
Pyridine	89.5	5.1	5.17	101.2
SERIES 1; a = + 0.1249				
Trimethylamine	88.0	2.38	2.197	92.3
Benzylamine	127.4	10.5	9.96	94.9
SERIES 8; a = -0.2219				
SERIES 7; a = -0.2799				
SERIES 6; a = -0.3468				
Dimethylamine	66.3	0.588	0.573	97.5
n-Amylamine	127.5	(7.30)[1]	6.00	(82.2)
Triethylamine	152.6	16.00	15.72	98.5
SERIES 5; a = -0.4260				
SERIES 4; a = -0.5229				
Methylamine	43.0	0.171	0.173	101.0
Ethylamine	64.6	0.396	0.397	100.2
Diethylamine	109.3	2.20	2.21	100.4
Piperidine	108.8	2.15	2.17	100.9
SERIES 3; a = -0.6478				
SERIES 2; a = -0.8439				

1 - Note that in Table V the perfect ratio 5 indicates identical behavior in bot xylene and chloroform; consequently the extraordinarily high value may reasonably be attributed to impurities.

Table IV.

The Partition Coefficients of the Acids, by SERIES; Chloroform.

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 3; a = +0.8095				
SERIES 2; a = + 0.6335				

(Table IV cont.)

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 1; a = +0.3324				
Benzoic acid	126.9	2.65	2.80	105.8
SERIES 8; a = +0.2355				
Caproic acid	152.5	6.10	6.27	102.8
SERIES 7; a = + 0.17754				
SERIES 6; a = + 0.1100				
n-Valeric acid	130.0	1.90	1.89	99.5
Piperonylic acid	148.7	4.00	3.87	96.8
iso-Caproic acid	152.0	4.60	4.39	95.5
Anisic acid	156.5	5.50	5.23	95.2
Hydrocinnamic acid	170.1	8.40	8.81	105.0
SERIES 5; a = + 0.0308				
SERIES 4; a = -0.0655				
n-Butyric acid	107.8	0.530	0.540	102.0
Salicylic acid	130.6	1.30	1.29	99.3
SERIES 3; a = -0.0904				
Formic acid	41.5	0.031	0.0317	102.2
Acetic acid	64.0	(0.0725)	0.0752	103.7
Propionic acid	85.3	0.163	0.170	104.3
α -Crotonic acid	102.1	0.34	0.324	95.4
sec.-Butyric acid	107.3	0.385	0.396	102.9
β -Iodopropionic acid	115.0	0.515	0.532	103.2
iso-Valeric acid	129.5	0.91	0.928	102.0
o-Chlorobenzoic acid	143.3	1.60	1.577	98.6
Phenylacetic acid	148.9	1.95	1.955	100.2
o-Iodobenzoic acid	159.4	2.92	2.926	100.2
SERIES 2; a = -0.3665				
α -Bromopropionic acid	105.8	0.248	0.249	100.3
m-Nitrobenzoic acid	151.9	1.46	1.462	100.1
p-Nitrobenzoic acid	152.5	1.50	1.497	99.7
SERIES 1; a = -0.66756				
Acetic acid	64.0	0.024	0.0251	104.6
Chloroacetic acid	78.0	0.0438	0.0429	97.9
Bromoacetic acid	84.5	0.0560	0.0550	98.2
Pyruvic acid	85.3	0.0592	0.0567	95.7
α-β-Dibromopropionic acid	127.8	0.280	0.290	103.6

(Table IV cont.)

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 8; a = -0.7644				
SERIES 7; a = -0.8224				
SERIES 6; a = -0.8894				
SERIES 5; a = -0.9686				
SERIES 4; a = -1.0655				
Anthranilic acid	135.0	0.148	0.153	103.3
3.5-Dinitrobenzoic acid	175.8	0.68	0.732	107.5
SERIES 3; a = -1.1904				
Lactic acid	88.7	0.0198	0.0194	98.0
o-Nitrobenzoic acid	150.8	0.225	0.0210	93.4
SERIES 2; a = -1.3665				
Laevulinic acid	130.0	0.063	0.0631	100.1
SERIES 1; a = -1.6675				
Succinic acid	120.0	0.020	0.0215	107.7
Benzilic acid	238.3	2.12	2.01	94.8
SERIES 8; a = -1.7644				
SERIES 7; a = -1.8224				
SERIES 6; a = -1.8894				
Gentisinic acid	136.5	0.0236	0.0243	103.0
Glutaric acid	142.2	0.029	0.0302	104.1
2.4-Dinitrobenzoic acid	175.3	0.000	0.1077	107.7
SERIES 5; a = -1.9686				
- - - - - - - - - -				
SERIES 2; a = -2.3665				
Camphoric acid	205.7	0.120	0.1153	96.3
			Average	100.8

Partition Coefficient Ratio

One of the conditions imposed upon our method of correction was that the ratio $\frac{P \text{ chloroform}}{P \text{ xylene}}$ should be a constant. We can see now how

this comes about. If we suppose that every compound falls in the same SERIES in chloroform as it did in xylene, the ratio between the partition coefficients into the two solvents should always be 5.0, because, as has been said, a particular SERIES in chloroform has a value of P at a given volume just five times its value at that same volume in xylene. But from Table V we see that this ratio is not always 5.0, but varies through a series of apparently related numbers running from 1.00 to 7.5. This is because compounds do not always fall in the same SERIES in the two solvents. The possible ratios are limited, however, because the number of possible SERIES are limited, and we may calculate the possible ratios on the basis that a compound may slip from any series in xylene to any series in chloroform. It is only necessary to consider one OCTAVE, for as a matter of fact, compounds never slip out of one OCTAVE. If we let n_x represent the SERIES number in xylene, and n_c the SERIES number in chloroform, the possible ratios are given by the formula

$$5 \frac{n_c}{n_x} = r$$

The 5 in the numerator is necessary because of the relative values of a particular SERIES in the two solvents. The possible ratios have been tabulated below:

	n_x				
	1	2	3	4	6
1	5.0	2.5	1.66	1.25	0.833
2	10.0	5.0	3.33	2.50	1.66
3	15.0	7.5	5.00	3.75	2.50
4	20.0	10.0	6.66	5.00	3.30
6	30.0	15.0	10.0	7.50	5.00

Table V.

Partition Coefficients Ratios:	P Xylene	P Chloroform	Chloroform / Xylene Nx	Nc	P Chloroform / P Xylene ( ) or 5 Nc/Nx
Gentisinic acid	0.0242	0.0236	3	6	0.976
Bromoacetic acid	0.033	0.056	3	1	1.69
α,β-Dibromopropionic acid	0.168	0.280	3	1	1.66
p-Nitrobenzoic acid	0.90	1.50	6	2	1.66
Succinic acid	(0.0123)[1]	0.020	3	1	1.66
Salicylic acid	0.650	1.30	1	4	2.0
Acetic acid	(0.010)[2]	(0.025)[3]	2	1	2.50
Benzoic acid	1.10	2.65	2	1	2.41
sec-Butyric acid	0.160	0.385	6	3	2.41
α-Bromopropionic acid	0.095	0.248	4	2	2.61
Camphoric acid	0.048	0.120	3	2	2.50
o-Chlorobenzoic acid	0.635	1.60	6	3	2.52
α-Crotonic acid	0.135	01340	6	3	2.52
o-Iodobenzoic acid	1.15	2.92	6	3	2.54
α-Iodopropionic acid	0.208	0.515	6	3	2.48
Laevulinic acid	0.0242	0.063	4	2	2.60
Propionic acid	0.066	0.163	6	3	2.47
Pyridine	1.95	5.1	4	2	2.62
Pyruvic acid	0.0235	0.0592	2	1	2.52
Anisic acid	1.80	5.50	1	6	3.06
Hydrocinnamic acid	2.75	8.40	1	6	3.05
Piperonylic acid	1.29	4.0	1	6	3.07
Valeric acid	0.635	1.9	1	6	2.99
n-Butyric acid	0.158	0.53	6	4	3.31
Methylamine	0.051	0.171	6	4	3.35
Phenylacetic acid	0.52	1.95	4	3	3.75
n-Amylamine	1.46	7.3	6	6	5.00
Diethylamine	0.44	2.2	4	4	5.00
Dimethylamine	0.12	0.588	6	6	4.90
Ethylamine	0.077	0.396	4	4	5.15
Piperidine	0.44	2.15	4	4	4.90
Triethylamine	3.17	16.00	6	6	5.07
Trimethylamine	0.47	2.38	1	1	5.00
Benzylamine	1.4	10.5	6	1	7.50

1 - Calculated from ether, ratio 10 to 1; Cf. p. 2, Sec. 1, Chandler.
2 - Calculated from toluene, ratio 1 to 1; Cf. p. 2, Sec. 1, H. and F.
3 - Cf. p. 2, Sec. 1, chloroform, D. and G.

Space does not permit of a discussion of all the constitutive relations involved in these partition coefficients ratios, but a few of the more important points need to be emphasized.

It will be recalled that most of the aliphatic amines and the unsubstituted aliphatic acids fell in SERIES 6 in xylene. In chloroform we find the amines in SERIES 6 again, hence the ratio 5.0; the acids, however, occur in SERIES 3, reducing the ratio to 2.5. It was further pointed out that the acids from valeric or in the case of xylene, slipped up a SERIES with each succeeding member. In chloroform we see that this slipping process is repeated, but it begins with one member earlier in the group, namely with butyric acid. Thus formic, acetic and propionic acids appear in SERIES 3, butyric acid in SERIES 4, valeric acid in SERIES 6. (Notice how valeric acid again avoids the blank SERIES 5).

Several reasons have already been given for believing that these SERIES numbers indicate the relative intrinsic intensity of secondary valence of the respective molecular species. This intensity, we have seen, depends upon the chemical constitution of the molecule and changes as a result of internal interactions between the component atoms. Now we see that this intensity is influenced not only by the chemical constitution of the molecule, but also by the environment. For though the same sample of butyric acid was used in determining the partition coefficient into xylene

chloroform, it does not behave in the same way towards the two solvents. In the former instance it fell in the same SERIES as the preceding acids; in the latter instance, like valeric acid, it leaves the company of the preceding acids to pass into the next SERIES. Numerous other instances of this same kind could be cited, all of which indicate some as yet obstruse but definite principle underlying constitutive behavior. It is significant, however, that all these changes are in accordance with the SERIES behavior, the OCTAVE distribution and some unformulated, yet obviously systematic relationship dependent upon chemical constitution.

But one important thing can be learned from these facts, and that is that

> the intensity of secondary valence associated with a particular molecular species depends not only upon its chemical constitution, but also upon the nature of its environment.

What Constitutes Environment?

In both of the systems which have thus far been considered, we have as components water and an immiscible liquid, with the solute distributed between them. It might be admitted that sufficient chloroform could dissolve in the water to cause these profound changes in the solute, but it is difficult to understand how xylene could exert any such influence in this manner, for it is quite insoluble. But in both cases the second liquid is always intermolecularly connected, so to speak, with the water through the interfaces and

through the mutually contained solute. It must be through these channels, then, that equilibrium is established in such a system. The system consists of many molecular parts, each part capable of internal changes, evoked by external influences; every part in delicate equilibrium with every other part.

Thus it is necessary to recognize an "equilibrium in state" for liquids: an equilibrium between the electrons in the atom and the forces acting between molecules. If this equilibrium is disturbed at any point through the introduction of a molecule of a dissimilar substance, a strain will be transmitted throughout the system, affecting in turn every other part. In view of these facts it is preposterous to suppose that the sole force involved in the distribution of a solute between two regions of a liquid, or between two immiscible liquids, is "gaseous diffusion pressure". The processes of diffusion and osmotic pressure appear to be consequences of the law of free energy working itself out through this molecule to molecule mechanism, distributing the strain in some definite manner in compliance with the nature of the electrical forces involved. At equilibrium, the system must possess a homogeniety of state, if we may call it that, for otherwise under the law of free energy relations the dissimilar molecules would be forced to the interfaces, and out of the system.

The facts which have been presented in this chapter throw some light on the relations of the solute to its environment, and on the question of what constitutes this environment. The nature of thes relations is held to be the most important fact, apart from the role of molecular volume itself,

disclosed by a study of partition coefficients:

> In any liquid system, all the parts of which are in cohesive contact, there exist equilibrated intermolecular forces involving all the contained molecules.

These forces have been shown to vary in a rhythmic manner, the observed variations being attributable both to internal (constitutive) and to external (environmental) influences.

> Thus a condition of equilibrium or compensation exists between the electrical mechanisms within the molecule (or its contained atoms) and the electrical forces which constitute its environment.

This equilibrium is not effected through gross electromagnetic laws, but through some as yet unpostulated rhythmic mechanism involving the valence electrons.

Chapter V.

THE PARTITION COEFFICIENTS INTO ETHER

In the preceding chapters the most essential points concerning molecular behavior have been developed. In the first place we have seen that, insofar as size is concerned, MOLECULAR VOLUME conditions molecular behavior. The next consideration, in order of importance, is the fact that various molecular species differ from each other in intensity of secondary valency by integrally related amounts. And third, that the behavior of a particular molecular species is determined not only by its intrinsic chemical nature, but also, and to an equally important degree, by the nature of its environment.

It is hardly necessary to point out that these facts are in direct contradiction to the current notions appertaining to the theory of solution, and that each of them is essentially new and recorded for the first time.

Space does not permit a discussion of the application of these facts to the gaseous theory of solution, and since we are dealing here with facts and not with theory, it is not incumbent upon us to consider for the time being, at least, any evidence other than that presented by direct experimentation. The revolutionary and profoundly fundamental nature of these disclosures brings, however, a grave responsibility; they have been obtained through the use of an unexplained and empirical method of correction applied to partition coefficients, and one

immediately wonders if this method of correction will be applicable under all circumstances. To what degree is it dependent upon the fact that water, supposedly so erratic in its physical behavior, is one of the solvents? To what extent does it satisfactorily dispose of the extremely complex relations of the mutual solubility of the two solvents, and the consequent changes in volume of the two solvent layers which may take place? It devolves upon us to answer these questions, and to further establish the validity of the method of correction before we can seek an explanation of the observed phenomena.

Ether offers us an opportunity for disposing of the question of the mutual solubility of the solvents; for at 25° water dissolves about 6 per cent of ether, and ether dissolves about 1 per cent of water. This is about ten times the mutual intersolubility of water and chloroform. Furthermore, ether is a better extractive of organic acids than the solvents previously used, and we are thus enabled to study many substances which could not be studied in the case of xylene or chloroform.

The fundamental relations disclosed by the partition coefficients between water and ether are in every respect identical with those disclosed by chloroform and xylene. Several additional points are brought out which will be considered in more detail later.

In Table VI the partition coefficients of the acids have been accorded the same treatment as in the previous tables. They are arranged by SERIES, and a glance at the last column of these tables will show the extent of the agreement between the "ideal" and the observed

values. The SERIES constants are based upon the more or less apparent fact that the ratio $\frac{Ps\ (ether)}{Ps\ (xylene)}$ at a given volume is 15.0. Thus the constant for any SERIES in ether is the sum of the constant for that same SERIES in xylene and the log of 15.0.

Table VI

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 3; a = + 1.2861				
Benzoic acid	126.9	25.0	25.2	101
SERIES 2; a = +1.1116	130.6	19.0	19.4	102.0
SERIES 1.1414; a = + 0.9605				
β -Iodopropionic acid	115.0	7.3	7.53	103.0
n -Valeric acid	130.0	13.5	13.40	99.3
SERIES 1; a = + 0.8095				
Formic acid	41.5	0.320	0.317	99.1
α -Crotonic acid	102.1	3.20	3.24	101.2
α -Bromopropionic acid	105.3	3.48	3.74	101.4
n-Butyric acid	107.8	4.00	4.04	101.0
o-Nitrobenzoic acid	150.8	2.17	2.103	96.8
SERIES 8; a = +0.7127				
Chloroacetic acid	78.0	1.02	1.03	101.0
Bromoacetic acid	84.5	1.32	1.32	100.0
Propionic acid	85.3	1.32	1.36	103.0
sec.-Butyric acid	107.3	3.22	3.17	98.5
iso-Valeric acid	129.5	7.40	7.43	100.3
Resorcinitic acid	136.3	9.4	9.64	102.3
o-Chlorobenzoic acid	143.3	12.5	12.60	100.8
Phenylacetic acid	148.9	15.2	15.6	102.5
o-Iodobenzoic acid	159.4	23.0	23.4	101.8
SERIES 7; a = + 0.6547				
m-Nitrobenzoic acid	151.9	15.5	15.4	99.4
SERIES 6; a = +0.5877				
Acetic acid	64.0	0.450	4.51	100.1
p-oxybenzoic acid	132.3	6.2	6.20	100.0

(Table VI cont.)

	Vm	P obs.	P calc.	P calc. / P obs.
SERIES 5; a = +0.5085				
α-β-Ditromopropionic acid	127.8	4.20	4.35	103.5
SERIES 4; a = +0.4116				
SERIES 3; a = +0.2867				
Gentisinic acid	136.5	3.6	3.64	101.1
m-Phthalic	156.7	8.0[1]	7.91	98.9
SERIES 2; a = +0.1096				
SERIES 1414; a = +0.0395				
α-Oxybutyric acid	111.2	0.633	0.651	102.8
3.5-Dinitrobenzoic acid	175.8	7.7	7.77	100.9
SERIES 1; a = -.1904				
Pyruvic acid	85.3	0.162	0.170	105.0
Anthranilic acid	135.0	1.11	1.147	103.3
SERIES 08. a = -0.2874				
Lactic acid	88.7	0.155	0.155	100.0
β-Oxybutyric acid	109.7	0.353	0.348	98.6
Trichloroacetic acid	119.5	0.495	0.506	102.2
SERIES 07: a = -0.3453				
SERIES 06: a = -0.4123				
Bromosuccinic acid	140.5	0.84	0.85	101.1
Mandelic acid	152.2	1.30	1.33	102.1
Acetylsalicylic acid	185.6	4.75	4.8	101.0
SERIES 05; a = -0.4915				
SERIES 04: a = -0.5884				
SERIES 03: a = -0.7133				
Malonic acid	97.8	0.077[1]	0.0825	(107.1)
Succinic acid	120.0	0.192	0.193	101.3
Laevulinic acid	130.0	0.280	0.284	
o-Phthalic acid	155.6	0.735	0.758	
SERIES 02; a = -0.8894				
2.4-Dinitrobenzoic acid	175.3	1.10	1.08	98.3
SERIES 01; a = -1.1904				
- - - - - - - - - - -				
SERIES 006; a = -1.4123				
Hippuric acid	178.7	0.379	0.368	97.2
- - - - - - - - - - -				

(Table VI cont.)

SERIES 003; a = -1.7133				
2.4.6-Trinitrobenzoic acid	197.0	0.36	0.371	103.0
Benzilic acid	238.3	18.0	18.1	100.5
			Average	

(1) Chandler, Loc. cit. Chart II.

The identification of the various SERIES is of course a matter of experiment. After five or six points have been found which obviously do not fall in the same SERIES, it can readily be seen that by graphical methods a complete OCTAVE may be laid down which includes all these points, and that there is only one possible solution of the problem. If by accident a SERIES is wrongly numbered, one or more of the observed points will fall between two SERIES lines. So after determining the position of any one SERIES by means of one or more points, it is only necessary to shift the OCTAVE until all the observed points are satisfactorily included in a SERIES.

Here, as in the case of xylene and chloroform, some SERIES seem to be more favored than others. Thus the distribution by SERIES is:

Series.	Acids No. of cases.	Amines. No. of cases.
1	7	2
2	1	0
3	9	1
4	0	3
5	1	0
6	6	7
7	1	1
8	12	0

In this case the behavior of the acids and amines differs considerably. It will be recalled that SERIES 5, 7 and 8 were blank in xylene and chloroform for both the acids and amines. In this case these SERIES are again blank for the amines with the exception of SERIES 7, which contains dimerthylamine. In the case of the acids, SERIES 4 is the only blank SERIES, but SERIES 2, 5 and 7 each contain only one compound. It is evident from this fact that we cannot describe any SERIES as being definitely blank; but that the appearance and identity of blank SERIES depend in some unexplainable way upon the nature of the solvents. It will be noticed in Table VI that an additional SERIES has been included; this is numbered SERIES 1.414 because it occurs midway between SERIES 1 and SERIES 2. The obvious simplicity of the 8 SERIES which constitute the OCTAVE, related to each other integrally as they are, leads one to question the existence of the intermediate SERIES; though some evidence of its existence was available in xylene and chloroform, it was insufficient to warrant recognition. In ether, however, we have four compounds occuring in

this SERIES; these, together with the other instances mentioned, are given below:

		Ether	P obs.	P calc.
First OCTAVE	( )	β-Iodopropionic acid n-Valeric acid	7.3 13.5	7.53 13.4
Second OCTAVE	( )	β-Oxybutyric acid 3.5-Dinitrobenzoic acid	0.633 7.70	0.651 7.77
		Xylene		
First OCTAVE	( )	n-Caproic acid	2.37	2.11
		Chloroform		
Second OCTAVE		β-Oxybutyric acid	0.196	0.205

Six instances are certainly sufficient to establish the existence of this peculiar intermediate series. Where all other SERIES are related to each other integrally, this one is unique in being the logarthmic mean between SERIES 1 and 2: (Log 2.0+ Log 1.0 /2 = 1.414). It is, however, approximately related to SERIES 1 as SERIES 7 is to SERIES 5, i. e. 7/5 = 1.400, but whether this relation or the one previously given is its true relation to the other SERIES cannot be said at the present time.

It is not necessary to dwell upon the constitutive relations involved in the ether study at this time. We have already seen how the comparative behavior of the various molecular species differed in chloroform as compared with xylene, and it is not surprising to see many rearrangements

of a similar nature in ether. It may be mentioned, however, that this point is further substantiation of the fact that the nature of the environment plays a specific and by no means negligable role in determining molecular behavior.

Though the average discrepancy between the observed and the calculated values is no less than that in xylene and chloroform, the general agreement is much more satisfactory, for it can be seen from Table VI that in but few instances is the discrepancy greater than 2.5 to 3.0 per cent. Considering the volatile nature of ether, these results are indeed encouraging, and establish at least one of the points raised in the first part of this chapter, namely, that the influence of the mutual solubility of the solvents (water and ether) is eliminated by our method of correction. We may believe that so far as the role of molecular volume and the existence of these integrally related SERIES is concerned, we are dealing with universal, and therefore fundamental, phenomena.

Chapter VI.

THE PARTITION COEFFICIENTS BETWEEN GLYCERINE AND ACETONE.

In Chapter V attention was called to the fact that in all the experimental work thus far developed, water was one of the solvents used. It seemed essential to study a system free of water in order to establish the universal nature of the observed phenomena. For this purpose, glycerine and acetone were chosen [1]. The glycerine takes the part of the water and the acetone the part of the organic solvent. Special apparatus was designed to facilitate the handling of the glycerine. A glass pistol-shaped containor was devised; it consisted of a bulb of constant volume, analogous to the pistol grip, opening at an angle into a tube of larger volume, analogous to the pistol barrel. The glycerine was run directly from an aspirator into the bulb by means of a suitable delivery tube, and an equal volume of the acetone solution added. After shaking, the acetone, being the liquid of lesser density, could be withdrawn directly into a pipette. All solutions were made in the acetone and titrated with standard acid or alkali.

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1. A good grade of commercial glycerine was heated to 140° C for two hours in order to dehydrate it and to expel any carbon dioxide present. The acetone was distilled over a mixture of calcium hydroxide and calcium chloride, and both the glycerine and acetone were protected from atmospheric moisture and carbon dioxide by calcium chloride- calcium hydroxide tubes

At the time of writing, the experimental work with this system is incomplete, and will therefore not be presented in detail. Several features in the behavior of the acids merit preliminary mention, however. In the first place, the general picture is the same as it was in the case of xylene: water, chloroform: water and ether: water in every respect. The function of volume is the same (see Equation I), and the inter-relations of SERIES are the same. There are thus far four compounds in the intermediate SERIES 1.414, thus substantiating its existence. The other compounds are distributed among SERIES as follows:

SERIES number	No. obs. cases
1	7
1.414	4
2	0
3	4
4	0
5	2
6	4
7	0
8	1
Total	22

Again certain SERIES appear to be favored and other SERIES appear blank, but there is hardly sufficient evidence to warrant discussion of this phase of the problem.

After shaking equal volumes of acetone and glycerine together, the acetone layer loses about 12 - 15 per cent in volume and the glycerine layer gains an equivalent amount. Here, then, is a situation which puts our method of correction to even a more severe test than the system ether: water.

For we are not determining the partition coefficient of the solute between pure acetone and pure glycerine, but between two layers of approximately respective compositions: 85% glycerine: 15% acetone and acetone containing a trace of glycerine. The decrease in volume of the acetone layer would necessitate an increase in solute concentration were the solute unable to pass into the glycerine layer. Thus the problem is extremely complicated, but the results indicate that so long as we deal with concentrations per unit volume of solvent and use the extrapolation method of correction, these complicating factors are automatically, though in an unexplainable fashion, eliminated.

A further substantiation of the method of correction is obtained in this system; the ratio $\frac{C \text{ acetone}}{C \text{ glycerine}}$ is for most of the aliphatic acids nearly a constant. It is, therefore, not necessary to apply any method of correction whatever, for the constancy of this ratio indicates that there is, in such instances, either no dissociation or association in either solvent; or, if dissociation or association exists, they change with dilution at the same rate in both solvents. The former supposition seems to be the most likely. But with some of the aromatic acids this ratio increases at an extremely rapid rate with increasing dilution, indicating either great dissociation in the acetone or great association in the glycerine. Without the method of correction now in use, compounds of such dissimilar behavior could never be compared; with this method of correction the behavior of these two types of compounds is not only brought into agreement, but it proves to be identical with the behavior manifested in the systems previously studied where dissociation and association were always in evidence. This is,

perhaps, the most important evidence so far obtained that the method of correction does for us just what was previously claimed: namely, that it eliminates all disturbing or complicating features, such as dissociation, association, and hydration from partition coefficient data, and renders them available for legitimate comparison.

Another point which can be discussed but tentatively at this time is the fact that under certain conditions of chemical constitution a solute will pass quantitatively into one or the other solvent. Having found that there exist several SERIES indicating differences in secondary valence, it might be expected that an unlimited number of such SERIES could exist, and that to obtain compounds in all SERIES was merely a matter of variation in chemical constitution. The first intimation that there exists a limiting SERIES, beyond which the solute will pass quantitatively into one or the other solvent, was encountered in the xylene; water system. It was noted that the dibasic acids were not extracted from water to the calculated or even to an appreciable extent by xylene. At the same time this fact was in part attributed to experimental difficulties and the matter was left in abeyance. The situation is reversed in the acetone: glycerine system, however, for many compounds are extracted quantitatively from glycerine by acetone (It will be recalled that the glycerine plays the part of the water in that it is the most polar solvent). As an example of this limiting SERIES we may mention the following; propionic acid occurs in SERIES 6, sec.butyric in SERIES 8, n-butyric in SERIES 1, and iso-valeric in SERIES 1.414; we would therefore expect to find n-Valeric in SERIES 2,

where it would have a partition coefficient of about 59.0 - a determinable value. Contrarily, it passes entirely into the acetone, giving a partition coefficient of infinite value. It is thought that in this same way the dibasic acidóhad partition coefficients in xylene of infinitisimal value. That such limiting conditions should exist is after all not surprising when one ponders over the possible mechanism of secondary valence and its discontinuous nature.

A further discussion of these and other extremely interesting points must be deferred until the experimental work is completed. Sufficient evidence is at hand to show that the phenomena with which we are concerned are universal, and that they have their origin in some fundamental mechanism which is more fundamental than atomic structure itself.

Chapter VII

DISCUSSION

The accummulation of experimental data serves no ultimately profitable end unless we can deduce from those data some simple truth which can be succinctly expressed; and which will serve to guide us in the analysis of other uncorrelated facts. It is my intention, therefore, at the risk of committing grave and costly errors, to marshal the facts which have been previously set forth into three principles. These principles have appeared to me as consequences of the experimental data; but I hope that to others the experimental data will appear as consequences of these principles.

I. The Principle of Homogeniety and Three Dimensional Symmetry.

In Chapter I it was shown that the experimental facts relating to the molecular volumes of liquid chemical compounds indicate that every molecule, no matter what its chemical configuration, completely fills (or occupies) a space which is symmetrical in three dimensions. Furthermore, that in a homogenous liquid, there is no "dead space", - no intermolecular interstices; chemical configuration is nothing more than a graphical delineation, and that, physically, a glass of water is "solid water" through and through.

The electrons and corpuscles in a glass of water completely fill, in a dynamic sense, the water domain, just as the molecules of a gas completely fill a room, in equilibrium at all points, and leaving not a

single crevice of "dead space" wherein the smallest body may be inserted without disturbing this equilibrium.

We have seen that molecular volume is a determining factor in homogenous liquid systems and we must reason that equilibrium and homogeniety are maintained at all times, regardless of the nature of the molecular species involved.

Out of these facts then, our first principle is forced upon us: every molecule in a homogenous liquid phase behaves toward its environment as though it completely fills a definite space which is symmetrical in three dimensions; this molecular domain is in contact on all sides with other and similar domains.

II. The Principle of Integrity.

The evidence has disclosed that the characteristic intensity of secondary valence associated with various molecular species differs by definite and integrally related amounts. This intensity is determined by the chemical constitution of the species under investigation and by the nature of its environment. This phenomenon is displayed by all types of compounds so far studied; compounds containing carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine and sulphur, in a large variety of chemical combinations. Consequently the fundamental picture, i. e. the existence of these integral relationships, cannot be attributed to peculiarities in molecular or atomic structure, but must be attributed

to something more fundamental than atomic structure itself, and something common to all atomic species: the nature of the fundamental electric charges.

The facts in the case leave us no choice in the formulation of the second principle: every molecule in a homogenous liquid phase behaves toward its environment as though it were a single electric charge, subject to definite but variable constraints, and occupying a volume equivalent to the molecular volume.

III. The Quantum Theory.

The assumption that the forces acting between the electron and the positive corpuscle are discontinuous in nature dates back, in a sense, to the first atomic theory based upon these discreet electrical bodies. It was a consequence, first, of the fact that the electron does not rush into and destroy the corpuscle; and secondly, of the necessity of postulating stable states, or rings or shells, etc., to account for atomic structure and the existence of the periodic relations among the elements. This assumption was given clearer definition, and was essentially established through the successful application of the quantum theory in all branches of physics.

In consequence of the quantum theory, one may believe that, for some as yet untold reason, every electron under the influence of a positive corpuscle is constrained to move through a series of"stable states".

These "stable states" constitute mathematically rigid constraints and they make possible the elaborate structures of atoms and molecules; they are, so to speak, the electrical beams and joists which cement together the electrical bricks in these superstructures. Having once introduced into electronic and corpuscular behavior a rigid constraint of this nature, it is inconceivable that by any possible permutation, it integrality can be destroyed. In every atom or molecule, no matter how complex the electronic-corpuscular fabrication, every electron must be similarly constrained, and no electron is free to move independently of the rest. All molecular behavior such as changes in state (e. g. solid, liquid and gas), as well as the changes in secondary valence as exemplified in this research, must ultimately be traced back to changes in the electronic-corpuscular fabrication of the molecule. And since electronic corpuscular fabrication is based upon a rigid and unitary constraint, it follows that changes in molecular behavior will be abrupt or discontinuous. Thus, in the behavior of the molecule we will have a replica of the behavior of a single electron, insofar as changes in state (or electrical constraint) are concerned. Or, in the words of the principle of integrity, every molecule will behave as though it were a single electron, subject to definite but variable constraints, and the degree of these constraints will be determined by the chemical constitution of the molecule.

Thus two molecules will behave toward each other as though they were point charges, and since no stipulations concerning directions have

been made, from an electro-dynamic point of view they will appear the same from all directions: c. g. they will possess three dimensional symmetry. Any number of such molecules, gathered together in positions of equilibrium with regard to each other will, for the same reasons, behave toward their environment as though they constituted a point charge, surrounded by a homogenous field symmetrical in three dimensions.

Thus homogeniety, three dimensional symmetry and integrity in behavior can be made to appear as inductive consequences of the assumption that the discreet electrical charges are united by rigid constraints. This assumption we have in the quantum theory, but it remains for the future to show why a rigid constraint exists.

Nor is it clear why two molecules should, at the critical pressure and temperature, unite to form a liquid. We cannot describe the mechanism by which this union takes place by resorting to continously diminishing forces, or stray electric fields, or to any of the other conceptions upon which we have previously relied. It is indeed apparent that we are very little nearer an understanding of the "nature of secondary valence". But in tearing down some of the old buttresses, we are perhaps preparing a place where a new and better structure may be reared.

Section I.

Benzene	25°	C_1	C_2	C_2/C_1	P	Reference[1]
Acetic acid	25°	m/10 cc	m/10 cc			
		32.98	2.559	0.0776		
		25.867	1.580	0.061		
		13.821	0.554	0.040	1m/10 cc	
		5.793	0.159	0.027	0.054	H. and F.
Chloroacetic acid	25°	71.856	3.177	0.0442		
		63.916	2.533	0.0396		
		21.191	0.729	0.0344	1m/10 cc	
		16.049	0.522	0.0325	0.0365	H. and F.
Phenol	25°	m/cc	m/cc			
		0.3660	2.978	8.13		
		0.2578	1.254	4.87		
		0.1013	0.279	2.75	1m/cc	
		0.0272	0.062	2.29	4.3	R. and W.
Pyridine	25°	m/.05 cc	m/.05 cc			
		0.000380	0.00110	2.9		
		0.000208	0.000546	2.62	1m/10 cc	
		0.000112	0.000274	2.50	2.6	H. and S.
Trimethylamine	25°	m/10 cc	m/10 cc			
		2.474	1.237	0.500		
		1.377	0.670	0.486	1m/10 cc	
		0.584	0.295	0.505	0.5	H. and F.
BROMOFORM						
Acetic acid	25°	m/cc	m/cc			
		10.2	2.062	0.202		
		8.74	1.430	0.164	1m/cc	
		5.37	0.593	0.110	0.148	H. and L.
Ammonium	25°	m/cc	m/cc			
		6.30	0.235	0.0373		
		4.18	0.131	0.0312	1m/10cc	
		2.59	0.070	0.0271	0.029	H. and L.

		C_1	C_2	C_2/C_1	P	Reference[1]
Chloroacetic acid	25°	m/cc	m/cc			
		9.69	1.20	0.124		
		9.61	0.813	0.084	1m/cc	
		8.85	0.649	0.073	0.094	H. and L.
Phenol	25°	m/cc	m/cc			
		0.364	2.70	7.42		
		0.304	1.80	5.89	1m.cc	
		0.109	0.322	2.96	4.3	H. and L.
Picric acid	25°	m/10 cc	m/10 cc			
		0.874	1.140	1.69		
		0.575	0.671	1.51	1m/10 cc	
		0.475	0.655	1.38	1.6	H. and L.
CARBON TETRACHLORIDE						
Acetic acid	25°	m/cc	m/cc			
		9.69	1.07	0.110		
		7.98	0.725	0.091	1m/cc	
		4.87	0.292	0.060	0.10	H. and L.
Chloroacetic acid	25°	m/cc	m/cc			
		11.3	0.551	0.0486		
		11.1	0.443	0.0398		
		10.7	0.362	0.0339		
		10.3	0.234	0.0229	1m/cc	
		9.6	0.159	0.0166	0.06	H. and L.
Phenol	25°	m/cc	m/cc			
		0.489	1.47	3.01		
		0.213	0.141	0.065	1m.cc	
		0.140	0.072	0.0514	2.45	H. and L.
CHLOROFORM						
Acetic acid	25°	m/cc	m/cc			
		2.056	0.349	0.169	1m/cc	
		1.527	0.207	0.136	0.20	
		1.188	0.135	0.114	1m/10 cc 0.10	R. and W.
	20°	0.2696	0.01222	0.0453		
		0.1946	0.007586	0.0390		
		0.1269	0.00406	0.0320	1m/1000cc	
		0.06445	0.00174	0.0270	0.025	D. and G.

		C_1	C_2	C_2/C_1	P	Reference
Ammonium	20°	gm/L	gm/L			
		7.861	0.2991	0.038		
		6.393	0.2439	0.038	1m/10 cc	
		5.160	0.1958	0.038	0.038	D. and C.
Chloroacetic acid	25°	m/cc	m/cc			
		7.70	0.840	0.109	1m/cc	
		7.23	0.707	0.0979	0.125	
		6.96	0.603	0.0866		
		3.65	0.253	0.0694	1m/10cc	
		1.05	0.061	0.0590	0.062	H. and L.
Phenol	25°	m/cc	m/cc			
		0.330	3.360	10.2		
		0.247	1.850	7.47	1m/cc	
		0.163	0.761	4.68	5.5	H. and L.
Picric acid	25°	m/10cc	m/10cc			
		0.561	1.41	2.52		
		0.488	1.09	2.23	1m/10cc	
		0.329	0.547	1.66	2.2	H. and L.
TOLUENE						
Acetic acid	25°	m/cc	m/cc			
		5.401	0.4477	0.0828		
		2.063	0.0864	0.0418		
		1.117	0.0343	0.0293	1m/1000cc	
		0.334	0.0060	0.0181	0.0101	H. and F.
	25°	m/10cc	m/10cc			
		95.10	12.69	0.136	1m/cc	
		62.61	5.75	0.0919	0.12	H. and F.
Chloroacetic acid	25°	m/10cc	m/10cc			
		92.04	5.434	0.059	1m/cc	
		80.68	3.358	0.0416	0.07	
		54.50	1.699	0.0312	1m/10cc	
		33.46	0.926	0.0277	0.028	H. and F.
Phenol	25°	m/10cc	m/10cc			
		4.75	14.96	3.15	1m/cc	
		2.20	4.66	2.12	2.75	H. and V.

		C_1	C_2	C_2/C_1	P	Reference
Pyridine	25°	m/cc	m/cc			
		0.0517	0.1129	2.18		
		0.0132	0.0275	2.08		
		0.0033	0.0066	2.00	1m/10cc	
		0.0007	0.0010	1.44	2.06	H. and V.
Trimethylamine	25°	m/cc	m/cc			
		0.0819	0.0363	0.443		
		0.0408	0.0177	0.433	1m/10cc	
		0.0206	0.0087	0.422	0.43	H. and V.

ETHER[2]	C_1 m/cc	C_1/C_2	Average value $C_1/C_2(1-a)$	P
Oxalic acid	0.1339	17.77		
	0.0887	21.66		
	0.0198	42.54		
	0.0103	61.38		
	0.0054	100.00	8.64	0.03
Malonic acid	0.1478	10.94		
	0.1121	11.07		
	0.0862	11.28		
	0.0331	12.22	9.83	0.077
Succinic acid	0.0217	7.81		
	0.0121	7.95		
	0.0059	8.39		
	0.0039	8.42		
	0.0023	8.79	7.45	0.123
Glutaric acid	0.0280	3.72		
	0.0085	3.84		
	0.0072	3.91		
	0.0063	3.92		
	0.0056	3.93	3.58	0.253
Pimelic acid	0.0098	0.7095		
	0.00702	0.7170		
	0.00480	0.7195		
	0.00284	0.7480		
	0.00179	0.7075	0.664	1.39

	C_1 m/cc	C_1/C_2	Average value $C_1/C_2(1-a)$	P
Suberic acid	0.00986	0.215		
	0.00544	0.228		
	0.00175	0.246		
	0.00084	0.258		
	0.00049	0.274	0.212	3.45
Azelaic acid	0.00064	0.0782		
	0.00058	0.0800		
	0.00051	0.0810		
	0.00046	0.0823		
	0.00033	0.0888	0.0637	9.5
Maleic acid	0.0253	13.27		
	0.0196	14.40		
	0.0143	16.06		
	0.0100	17.78		
	0.0054	23.70	6.71	0.0668

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Only a part of Chandler's work is quoted in the above tables. The figures given in the third column for $C_1/C_2(1-a)$ are averages derived from a large number of concentrations. Note that in column 4 P C_2/C_1, not C_1/C_2 as given by C.

SECTION II.

The Partition Coefficients of the Acids between Water and Xylene, 25°.

	C_1	C_2	C_2/C_1	P
Acetylsalicylic acid	17.30	7.25	0.419	
	14.62	5.38	0.368	
	7.15	2.00	0.280	
	3.85	0.875	0.227	
	3.28	0.719	0.219	0.222
iso-Amylacetic acid	0.85	7.95	9.37	
	0.375	3.625	9.67	
	0.212	2.170	10.25	
	0.0792	0.8580	10.85	10.70
Anisic acid	0.682	1.50	2.20	
	0.467	0.700	1.50	
	0.381	0.494	1.30	
	0.243	0.195	0.802	1.80
Benzilic acid	1.252	0.975	0.788	
	1.029	0.643	0.625	
	0.757	0.363	0.479	
	0.448	0.133	0.300	0.800
Benzoic acid	4.19	17.4	4.15	
	1.568	2.90	1.85	
	0.842	0.865	1.03	
	0.794	0.819	1.03	
	0.737	0.678	0.92	1.10
Bromoacetic acid	37.40	1.15	0.0325	
	26.70	0.90	0.0337	
	23.30	0.70	0.0300	0.033
α-Bromopropionic acid	13.10	1.40	0.107	
	10.50	1.00	0.095	
	8.40	0.70	0.0835	
	6.20	0.44	0.071	0.095
Bromosuccinic acid	61.70	1.85	0.03	
	25.90	0.555	0.0214	0.0252
n-Butyric acid	8.20	1.30	0.159	
	6.475	1.025	0.158	
	4.500	0.700	0.156	0.158

	C_1	C_2	C_2/C_1	
sec.-Butyric acid	18.35	3.50	0.19	
	9.575	1.625	0.17	
	3.65	0.575	0.157	0.160
Camphoric acid	19.166	0.834	0.0436	
	9.722	0.278	0.0286	
	3.922	0.0776	0.0198	0.048
n-Caproic acid	2.80	17.7	6.32	
	0.95	2.95	3.10	
	0.75	2.15	2.86	
	0.575	1.50	2.61	
	0.3375	0.7375	2.18	
	0.2625	0.5375	2.04	2.37
iso-Caproic acid	1.85	5.6	3.02	
	1.325	3.375	2.54	
	0.8125	1.6375	2.02	
	0.4625	0.7500	1.62	1.75
o-Chlorobenzoic acid	4.55	7.45	1.63	
	2.30	2.20	0.956	
	1.75	1.325	0.757	
	1.55	0.975	0.630	
	1.19	0.600	0.505	0.635
Cinnamic acid	0.295	2.215	7.45	
	0.225	1.025	4.55	
	0.160	0.465	2.90	4.50
α-Crotonic acid	13.9	2.5	0.180	
	6.3	0.80	0.127	
	4.75	0.55	0.115	0.135
α-β-Dibromopropionic acid	7.35	1.45	0.197	
	7.20	1.30	0.181	
	5.20	0.75	0.144	
	3.70	0.50	0.135	0.168
2.4-Dinitrobenzoic acid	10.95	1.10	0.100	
	8.60	0.70	0.0815	
	7.85	0.55	0.070	
	6.78	0.40	0.059	0.10
3.5-Dinitrobenzoic acid	4.05	4.50	1.11	
	3.15	2.95	0.936	
	2.40	2.10	0.875	
	1.53	1.11	0.720	0.70

	C_1	C_2	C_2/C_1	P
Gentisinic acid	37.50	0.95	0.024	
	30.50	0.61	0.020	
	23.55	0.40	0.017	0.0242
O-Iodobenzoic acid	1.10	2.20	2.00	
	0.60	0.55	0.916	
	0.325	0.175	0.538	1.15
β-Iodopronpionic acid	13.75	4.46	0.325	
	7.25	1.75	0.242	
	6.60	1.44	0.218	
	3.90	0.745	0.191	
	2.97	0.525	0.1765	0.208
Hydrocinnamic acid	1.15	5.00	4.35	
	0.85	3.40	4.00	
	0.575	1.775	3.09	
	0.375	0.975	2.60	2.75
Laevulinic acid	51.7	1.40	0.0271	
	26.0	0.50	0.0192	
	35.0	0.80	0.0228	0.0242
o-Nitrobenzoic acid	10.3	0.90	0.0874	
	7.6	0.70	0.0920	
	5.7	0.55	0.0965	
	3.925	0.425	0.1080	0.085
m-Nitrobenzoic acid (1st recrystallization)	2.85	3.25	1.14	
	2.30	2.30	1.00	
	1.85	1.60	0.865	
	1.325	0.95	0.818	0.73
m-Nitrobenzoic acid (2nd recrystallization)	3.00	3.35	1.11	
	2.20	2.10	0.955	
	1.60	1.375	0.860	
	1.20	0.850	0.708	0.74
p-Nitrobenzoic acid	1.10	0.950	0.864	
	0.962	0.7375	0.767	
	0.725	0.4625	0.638	
	0.681	0.4530	0.665	
	0.3825	0.1750	0.458	0.90

	C_1	C_2	C_2/C_1	P
Phenylacetic acid	5.00	5.00	1.00	
	3.50	2.473	0.708	
	2.60	1.5375	0.592	
	1.60	0.7750	0.484	
	1.26	0.5750	0.456	0.51
Phenylacetic acid	3.575	4.825	1.35	
(2 vols. xylene to	2.875	3.325	1.16	P C_2= 2m/L
1 vol. of water)	2.350	2.400	1.068	
	1.400	1.275	0.910	1.02
Phenylacetic acid	4.90	3.05	0.623	
(2 vols. water to	2.58	0.85	0.330	P C_2= 0.5m/L
1 vol. xylene)	1.75	0.35	0.200	
	1.18	0.175	0.148	0.253
Phthalic acid	38.60	1.70	0.0430	
	32.55	1.25	0.0384	
	14.45	0.35	0.0243	0.0355
Piperonylic acid	0.865	1.14	1.32	
	0.660	0.779	1.182	
	0.3595	0.3142	0.875	1.29
Propionic acid	19.30	1.30	0.067	
	9.20	0.60	0.065	
	3.80	0.20	0.0528	0.066
Pyruvic acid	63.7	1.85	0.029	
	45.8	1.10	0.024	
	19.6	0.40	0.0204	0.0235
Resorcinilic acid	40.5	1.50	0.037	
	26.8	0.80	0.0298	
	19.2	0.50	0.0260	0.032
Salicylic acid	4.675	5.675	1.215	
	3.075	3.075	1.000	
	1.785	1.238	0.692	
	1.350	0.862	0.638	
	0.038	0.550	0.530	0.650
n-Valeric acid	8.48	11.6	1.38	
	5.00	5.00	1.00	
	2.30	1.70	0.74	
	2.175	1.575	0.725	
	1.500	0.925	0.616	
	1.150	0.625	0.543	
	0.6625	0.3125	0.472	0.635

	C_1	C_2	C_2/C_1	P
iso-Valeric acid	6.15	3.15	0.512	
	5.30	2.60	0.490	
	4.275	1.925	0.450	
	3.85	1.55	0.403	
	2.35	0.875	0.372	
	1.875	0.600	0.320	0.370

The Partition Coefficients of the Bases between Water and Xylene, 25°.

Allylamine	6.50	1.30	0.200	
	3.30	0.55	0.196	
	1.85	0.35	0.189	0.198
n-Amylamine	5.08	14.92	2.94	
	2.655	7.17	2.70	
	1.875	4.275	2.28	
	1.466	3.05	2.18	
	1.335	2.67	2.00	
	0.755	1.15	1.52	1.46
iso-Amylamine	2.65	5.10	1.92	
	1.00	1.50	1.50	
	0.80	1.175	1.47	
	0.85	1.073	1.43	
	0.55	0.700	1.28	
	0.525	0.650	1.24	1.38
Anilin	0.378	2.00	5.3	
	0.297	1.20	4.3	
	0.203	0.67	3.3	
	0.150	0.45	2.9	4.00
Benzylamine	6.32	13.68	2.16	
	3.35	6.65	1.99	
	1.58	2.42	1.53	
	0.81	1.19	1.47	1.40
Benzylethylamine	1.40	18.60	13.4	
	0.70	9.30	13.3	
	0.35	4.65	13.3	
	0.141	1.86	13.5	
	0.103	1.368	13.6	13.4

	C_1	C_2	C_2/C_1	P
Benzylmethylamine	1.138	8.86	7.80	
	0.75	5.00	6.66	
	0.026	1.20	5.30	
	0.15	0.725	4.83	5.10
Bornylamine	0.00125	4.72	58.00	
	0.0570	3.16	55.50	
	0.0455	2.50	55.00	ca. 54.00
n-Butylamine	5.60	4.40	0.785	
	2.40	1.50	0.665	
	1.28	0.718	0.560	
	0.671	0.328	0.490	0.60
iso-Butylamine	3.575	2.075	0.58	
	1.775	0.975	0.55	
	0.625	0.362	0.58	0.58
Camphylamine	0.0625	3.587	57.9	
	0.0396	2.210	55.3	
	0.0182	0.882	54.0	ca. 54.2
Coniine	0.935	9.065	9.7	
	0.495	3.505	7.1	
	0.265	1.735	6.5	
	0.146	0.861	5.9	6.0
Diethylamine	12.68	7.42	0.59	
	6.45	3.55	0.552	
	4.075	1.925	0.472	
	2.950	1.30	0.441	
	2.72	1.28	0.470	
	1.95	0.75	0.410	
	1.45	0.55	0.380	0.44
Dimethylamine (in water)	17.78	2.22	0.125	
	8.97	1.12	0.125	
	3.55	0.420	0.121	
	1.786	0.214	0.120	0.125
Dipropylamine	2.42	17.58	7.25	
	1.45	8.55	5.90	
	0.85	4.15	4.88	
	0.575	2.325	4.04	
	0.456	1.544	3.38	
	0.425	1.525	3.59	
	0.323	1.04	3.19	3.15

	C_1	C_2	C_2/C_1	P
Ethylamine (in alcohol)	19.284	1.426	0.074	
	9.255	0.745	0.0805	
	3.654	0.346	0.0947	
	1.7955	0.2045	0.1140	0.077
n-Hexylamine	2.80	17.2	6.15	
	1.50	8.50	5.65	
	0.7775	3.225	4.17	
	0.625	2.325	3.88	
	0.425	1.3375	3.14	
	0.225	0.5875	2.61	3.05
n-Heptylamine	0.445	9.565	21.5	
	0.431	9,562	21.8	
	0.270	3.730	13.8	
	0.152	1.848	12.3	
	0.083	0.917	11.0	11.2
Methylamine (in water)	19.018	0.982	0.0517	
	9.499	0.501	0.0528	
	3.745	0.255	0.0680	
	1.730	0.130	0.0750	0.051
Methylanilin	0.300	3.40	11.3	
	0.185	2.10	10.9	
	0.125	1.31	10.5	10.45
n-Methylpiperidine	7.33	12.67	1.725	
	3.79	6.21	1.640	
	2.40	3.40	1.420	
	1.85	2.575	1.390	
	1.70	2.300	1.350	
	1.05	1.325	1.260	
	0.683	0.934	1.365	
	0.700	0.9375	1.340	1.20
Phenylethylamine	0.4125	1.51	3.64	
	0.3437	1.13	3.29	
	0.2380	0.763	3.20	
	0.1940	0.582	3.00	3.20

	C_1	C_2	C_2/C_1	P
Piperidine	7.00	4.00	0.57	
	3.725	1.975	0.53	
	2.850	1.300	0.456	
	2.500	1.200	0.480	
	1.850	0.750	0.406	
	1.25	0.450	0.360	0.440
Propylamine	7.75	2.25	0.290	
	4.80	1.30	0.270	
	2.45	0.60	0.246	0.26
Pyridine	9.75	19.00	1.95	
	4.80	9.50	1.98	
	2.05	3.80	1.85	
	1.00	1.90	1.90	1.95
Quinoline	0.470	9.40	20.0	
	0.250	4.20	16.8	
	0.116	1.80	15.5	14.0
Triethylamine	2.53	17.47	6.90	
	1.49	8.51	5.72	
	0.80	3.60	4.50	
	0.75	3.25	4.33	
	0.625	2.475	3.96	
	0.3875	1.412	3.57	
	0.3125	0.9875	3.16	3.17
Trimethylamine (in alcohol)	14.22	5.78	0.407	
	6.97	3.03	0.435	
	2.775	1.225	0.442	
	2.13	1.00	0.47	0.47
Xylidene, 1.3.4.	0.2875	3.3125	11.5	
	0.1385	1.525	11.0	
	0.1070	1.200	11.2	11.0
Xylidene, 1.4.3.	0.2875	4.462	15.5	
	0.1420	2.150	15.1	
	0.0740	1.100	14.9	14.9

The Partition Coefficients of Acids
Between Water and Chloroform, 25°.

	C_1	C_2	C_2/C_1	P
Acetic acid	20.9	2.00	0.0955	
	13.8	1.00	0.0725	
	8.35	0.45	0.0540	
	5.85	0.235	0.0400	0.0725
Anisic acid	0.025	1.75	6.36	
	0.206	1.206	5.85	
	0.162	0.875	5.38	
	0.125	0.625	5.00	5.50
Anthranilic acid	16.10	2.87	0.178	
	10.00	1.54	0.154	
	6.62	0.96	0.145	
	4.50	0.60	0.133	0.148
Benzilic acid	0.640	1.75	2.74	
	0.460	0.96	2.08	
	0.2305	0.2885	1.25	2.12
Benzoic acid	1.137	4.55	3.96	
	0.675	2.125	3.15	
	0.599	1.84	3.07	
	0.396	1.054	2.66	
	0.3025	0.732	2.42	
	0.2380	0.5625	2.36	2.65
Bromoacetic acid	32.00	2.08	0.065	
	18.45	1.05	0.0570	
	14.45	0.75	0.0519	
	9.40	0.45	0.0478	0.0550
α-Bromopropionic acid	20.20	5.56	0.276	
	13.00	3.48	0.268	
	6.65	1.70	0.256	
	4.40	1.10	0.230	0.248
n-Butyric acid	3.930	2.190	0.577	
	2.290	1.252	0.546	
	1.680	0.866	0.516	
	1.402	0.710	0.506	
	1.169	0.574	0.491	
	1.040	0.488	0.470	0.530

	C_1	C_2	C_2/C_1	P
sec.-Butyric acid	5.450	2.350	0.431	
	3.190	1.275	0.408	
	2.100	0.750	0.357	
	1.025	0.350	0.342	0.385
Camphoric acid	19.25	10.35	0.538	
	7.95	1.50	0.189	
	4.30	0.525	0.116	0.120
n-Caproic acid	0.2125	1.4375	6.77	
	0.1875	1.1375	6.08	
	0.1158	0.6344	5.49	
	0.0843	0.4281	5.07	6.1
iso-Caproic acid	0.4475	2.550	5.7	
	0.2900	1.450	5.0	
	0.2175	1.000	4.6	
	0.1710	0.755	4.38	4.6
Chloracetic acid	35.90	2.80	0.078	
	28.60	1.55	0.0543	
	16.10	0.50	0.0310	
	12.00	0.30	0.0250	0.0438
o-Chlorobenzoic acid	1.075	2.690	2.50	
	0.760	1.488	1.955	
	0.649	1.072	1.655	
	0.492	0.649	1.320	1.60
α-Crotonic acid	7.15	3.40	0.475	
	5.10	2.125	0.417	
	3.55	1.30	0.366	
	2.35	0.75	0.319	0.340
α-β-Dibromopropionic acid	4.98	1.63	0.327	
	3.54	0.985	0.278	
	2.66	0.560	0.210	
	1.85	0.313	0.169	0.260
2.4-Dinitrobenzoic acid	10.95	1.10	0.100	
	8.60	0.70	0.0815	
	7.85	0.55	0.0700	
	6.78	0.40	0.059	0.10

	C_1	C_2	C_2/C_1	P
3.5-Dinitrobenzoic acid	4.04	3.71	0.918	
	2.855	2.38	0.834	
	1.992	1.425	0.715	
	1.450	0.975	0.672	0.68
Formic acid (average value)	33.2	1.00	0.031	0.031
Gentisinic acid	38.40	0.90	0.0234	
	20.70	0.45	0.0217	
	15.20	0.32	0.0210	0.0236
Glutaric acid	33.1	0.905	0.0273	
	24.70	0.570	0.0231	
	17.90	0.375	0.0210	0.029
Hydrocinnamic acid	0.177	1.770	10.00	
	0.134	1.190	8.87	
	0.1058	0.835	7.90	
	0.089	0.650	7.30	8.40
o-Iodobenzoic acid	0.473	1.990	4.21	
	0.335	0.973	2.90	
	0.287	0.680	2.37	
	0.244	0.493	2.02	
	0.248	0.512	2.06	2.92
β -Iodopropionic acid	5.55	3.50	0.630	
	3.70	2.12	0.572	
	2.80	1.542	0.552	
	1.61	0.805	0.500	
	1.162	0.5375	0.462	0.515
Lactic acid	79.8	1.80	0.0226	
	50.4	1.00	0.0198	
	32.8	0.60	0.0183	
	26.9	0.43	0.0160	0.0198
Laevulinic acid	24.5	2.00	0.0817	
	18.55	1.35	0.0728	
	12.80	0.75	0.0586	0.063
o-Nitrobenzoic acid	8.65	3.35	0.388	
	6.60	2.05	0.310	
	5.55	1.55	0.279	
	2.775	0.45	0.162	0.225

	C_1	C_2	C_2/C_1	P
m-Nitrobenzoic acid	0.950	1.625	1.71	
	0.675	0.975	1.44	
	0.4874	0.600	1.23	1.46
p-Nitrobenzoic acid	1.05	1.975	1.88	
	0.75	1.175	1.57	
	0.525	0.687	1.31	
	0.364	0.400	1.10	1.50
Phenylacetic acid	0.715	1.542	2.16	
	0.518	1.1010	1.95	
	0.425	0.785	1.845	
	0.280	0.475	1.70	1.95
Piperonylic acid	0.250	1.0375	4.15	
	0.2187	0.8125	3.71	
		0.5812	3.32	4.00
Propionic acid	10.75	1.95	0.1818	
	7.12	1.175	0.165	
	2.92	0.40	0.137	
	5.65	0.85	0.153	0.163
Pyruvic acid	31.2	2.00	0.064	
	16.90	1.00	0.0592	0.0592
Salicylic acid	2.625	6.575	2.50	
	1.425	2.625	1.84	
	1.138	1.862	1.64	
	0.850	1.130	1.38	
	0.608	0.700	1.20	
	0.575	0.625	1.09	1.30
Succinic acid	48.00	0.95	0.0198	
	34.90	0.60	0.0172	
	20.50	0.30	0.0146	
	13.50	0.15	0.0110	0.020
Valeric acid	1.825	4.625	2.53	
	0.910	2.00	2.20	
	0.650	1.33	2.08	
	0.390	0.70	1.80	1.90
iso-Valeric acid	3.35	4.55	1.36	
	2.45	2.90	1.182	
	1.585	1.65	1.040	
	1.239	1.162	0.94	0.91

The Partition Coefficients of the Bases between Water and Chloroform, 25°.

	C_1	C_2	C_2/C_1	P
n-Amylamine	0.2000	2.30	11.5	
	0.1735	1.70	9.8	
	0.150	1.20	8.0	
	0.1168	0.6832	5.86	7.3
Benzylamine	1.20	19.6	16.3	
	0.65	9.55	14.7	
	0.30	3.85	12.0	10.5
Diethylamine	4.350	17.95	4.13	
	1.625	5.025	3.09	
	0.800	2.000	2.50	
	0.300	0.600	2.00	2.20
Dimethylamine (in water)	5.85	3.40	0.582	
	4.55	2.65	0.582	
	3.40	2.00	0.586	
	2.20	1.275	0.580	
	1.35	0.80	0.592	0.588
Ethylamine	25.50	20.70	0.78	
	18.45	9.45	0.512	
	10.20	4.80	0.470	
	4.30	1.80	0.418	
	2.525	1.00	0.396	
	1.50	0.55	0.366	0.396
Methylamine (in water)	27.4	4.5	0.164	
	13.5	1.9	0.141	
	6.15	1.225	0.199	(average)
	2.625	0.475	0.181	0.171
Triethylamine	0.425	0.575	22.5	
	0.194	3.806	19.7	
	0.0516	0.800	15.5	
	0.0375	0.490	13.0	16.0
Trimethylamine (in alcohol)	4.85	14.95	3.08	
	1.05	2.90	2.62	
	0.60	1.50	2.50	
	0.30	0.70	2.33	2.38

	C_1	C_2	C_2/C_1	P
Piperidine	1.725	6.225	3.61	
	1.200	3.625	3.02	
	0.643	1.556	2.42	
	0.400	0.800	2.00	2.15
Pyridine	1.45	16.25	11.2	
	0.55	5.10	9.3	
	0130	2.2	7.3	
	0.225	1.225	5.4	5.1

Section III.

The Partition Coefficients of the Acids between Water and Ether,, 25°.

	C_1	C_2	C_2/C_1	P
Acetic acid	14.4	6.75	0.468	
	8.90	4.20	0.472	
	5.20	2.35	0.452	
	2.8625	1.2875	0.449	
	1.075	0.475	0.442	0.450
Acetyl salicylic acid	1.32	8.84	6.7	
	0.84	5.16	6.15	
	0.49	2.75	5.62	
	0.31	1.57	5.06	
	0.205	0.96	4.70	4.75
Anthranilic acid	6.04	6.80	1.125	
	3.57	4.04	1.130	
	1.86	2.21	1.190	
	0.100	1.05	1.050	
	0.520	0.560	1.075	1.11
Benzoic acid	0.370	13.75	37.80	
	0.270	8.130	30.15	
	0.1575	4.8625	30.85	
	0.095	2.3850	25.15	
	0.065	1.6250	25.00	
	0.0375	0.9125	24.30	25.00
Benzilic acid	0.300	9.22	30.7	
	0.160	4.44	27.7	
	0.1200	2.72	22.65	
	0.0775	1.55	20.00	
	0.0500	0.83	16.60	18.00
Bromoacetic acid	4.25	9.55	2.245	
	3.05	6.30	2.063	
	1.475	3.475	1.760	
	1.3125	1.8375	11438	
	0.9625	1.3375	1.390	1.32
α Bromopropionic acid	1.30	9.50	7.30	
	0.8625	4.8625	5.64	
	0.5875	2.7875	4.75	
	0.40525	1.68125	4.02	
	0.3125	1.1250	3.60	3.42

	C_1	C_2	C_2/C_1	P
Bromosuccinic acid	6.80	8.90	1.31	
	3.50	3.85	1.10	
	2.00	1.925	0.963	
	1.3625	1.1625	0.853	
	0.63125	0.4500	0.712	0.84
n-Butyric acid	1.80	9.20	5.12	
	1.60	5.02	4.73	
	0.59	2.65	4.50	4.00
s-Butyric acid	11.0	2.6		
	7.2	1.625		
	4.2	0.975		
	2.1125	0.500		
	1.150	0.29375		3.22
Chloroacetic acid	7.80	13.40	1.718	
	4.60	6.70	1.455	
	2.85	3.70	1.299	
	1.9375	2.3375	1.208	
	1.40	1.55	1.108	1.020
o-Chlorobenzoic acid	1.360	9.68	26.80	
	0.250	5.67	22.65	
	0.1925	3.7075	19.30	
	0.145	2.415	16.65	
	0.100	1.300	13.00	12.5
α-Crotonic acid	3.52	11.6	3.30	
	1.68	5.48	3.26	
	1.24	3.92	3.16	
	0.85	2.73	3.21	
	0.54	1.70	3.15	
	0.52	1.60	3.08	
	0.32	0.95	2.96	3.20
α,β-Dibromopropionic acid	0.450	3.2625	7.25	
	0.350	2.1000	6.00	
	0.25625	1.13125	4.42	
	0.21875	0.85625	3.92	4.20

	C_1	C_2	C_2/C_1	P
2.4-Dinitrobenzoic acid	2.495	7.78	3.12	
	1.79	4.08	2.28	
	1.45	2.51	1.73	
	1.15	1.69	1.41	
	0.67	0.68	0.91	1.10
3.5-Dinitrobenzoic acid	0.365	6.395	17.5	
	0.295	3.885	13.2	
	0.225	2.655	11.8	
	0.1950	1.815	9.8	
	0.1325	1.0475	7.9	7.7
Formic acid	30.00	13.25	0.442	
	13.45	4.75	0.353	
	8.85	3.25	0.368	
	6.20	2.30	0.371	
	4.65	1.625	0.350	0.320
Fumaric acid	8.85	6.75	0.763	
	4.80	3.50	0.729	
	2.60	1.70	0.654	
	1.5125	0.8375	0.554	
	1.01375	0.4625	0.454	0.58
Gentisinic acid	1.12	11.92	10.65	
	0.83	7.65	9.22	
	0.60	3.98	6.64	
	0.41	2.07	5.05	
	0.31	1.205	3.89	3.6
Hippuric acid	8.04	2.80	0.348	
	4.66	1.70	0.364	
	2.58	0.98	0.380	
	1.42	0.56	0.394	
	0.855	0.355	0.415	0.379
o-Iodobenzoic acid	0.1010	2.640	26.2	
	0.0602	1.400	23.2	
	0.0400	0.861	21.5	
	0.0238	0.505	21.2	23.0

	C_1	C_2	C_2/C_1	P
β-Iodopropionic acid	1.44	15.22	10.6	
	0.900	8.66	9.6	
	0.500	4.64	9.3	
	0.280	2.26	8.1	
	0.175	1.275	7.3	7.3
Laevulinic acid	14.65	3.75	0.2575	
	10.10	2.65	0.2625	
	5.15	1.40	0.2725	
	2.57	0.725	0.2820	
	1.725	0.500	0.2900	0.2800
Lactic acid	28.3	5.10	0.180	
	15.7	2.70	0.172	
	9.35	1.525	0.163	
	5.95	1.000	0.155	
	3.95	0.550	0.139	0.155
Mandelic acid	5.225	8.525	1.63	
	3.225	4.825	1.495	
	2.100	2.95	1.405	
	1.070	1.475	1.380	
	0.885	1.175	1.330	1.30
m-Nitrobenzoic acid	0.240	6.812	28.8	
	0.130	4.260	23.7	
	0.135	2.905	21.5	
	0.005	1.875	19.7	
	0.075	1.250	16.7	15.5
o-Nitrobenzoic acid	1.840	13.08	7.11	
	1.200	6.96	5.80	
	0.790	3.035	3.84	
	0.543	1.413	2.60	
	0.379	0.663	1.75	2.17
o-Oxybenzoic acid	1.4	12.8	9.15	
	0.875	7.425	8.50	
	0.575	5.025	8.72	
	0.400	3.250	8.13	
	0.3125	2.2625	7123	ca. 6.2
α-Oxybutyric acid	9.70	6.40	0.660	
	8.75	3.55	0.617	
	4.1375	2.7125	0.656	
	2.875	1.875	0.652	
	1.7625	1.0875	0.617	0.633

	C_1	C_2	C_2/C_1	P
β-Oxybutyric acid	8.95	6.60	2.36	
	6.45	4.75	1.70	
	4.125	3.05	1.075	
	2.325	1.725	0.600	
	1.45	1.075	0.375	
m-Phthalic acid				8.00[1]
Phthalic acid	6.675	6.575	0.985	
	3.800	3.375	0.888	
	2.375	1.925	0.810	
	1.5375	1.100	0.716	
	0.96875	0.66875	0.690	0.735
Phenylacetic acid	1.08	16.12	15.0	
	0.44	7.44	16.9	
	0.26	3.82	14.7	
	0.17	2.47	14.5	
	0.085	1.255	14.7	15.2
Propionic acid	5.45	8.30	1.52	
	2.35	3.375	1.435	
	0.925	1.225	1.325	
	0.675	0.8875	1.315	1.32
Pyruvic acid	14.10	2.40	0.170	
	7.05	1.15	0.163	
	5.00	0.80	0.160	
	3.65	0.55	0.151	0.162
Resorcinilic acid	0.50	12.75	25.50	
	0.3875	8.7125	22.50	
	0.28125	4.51875	16.00	
	0.1550	1.5950	11.81	ca. 9.4
Salicylic acid	0.295	14.825	50.3	
	0.195	7.645	39.2	
	0.125	3.855	30.8	
	0.0850	2.415	28.4	
	0.0666	1.3975	21.0	19.0

	C_1	C_2	C_2/C_1	P
Succinic acid	13.8	2.75	0.199	
	7.95	1.55	0.195	
	4.3625	0.8625	0.1975	
	2.6250	0.4875	0.186	
	1.6000	0.2880	0.180	0.192
Trichloroacetic acid	7.10	10.40	1.465	
	5.10	5.40	1.060	
	3.20	2.50	0.781	
	1.95	0.85	0.436	
	1.4625	0.5625	0.385	0.495
2.4.6.-Trinitrobenzoic acid	8.28	5.88	0.710	
	4.80	2.20	0.458	
	2.56	0.84	0.328	
	1.09	0.200	0.182	ca. 0.36
Valeric acid	0.3900	5.6700	14.52	
	0.3000	4.3000	14.32	
	0.1700	2.2000	12.95	
	0.1125	1.4575	12.92	
	0.0775	1.0225	13.20	13.54
iso-Valeric acid	1.325	11.0	8.32	
	0.8875	7.0875	7.98	
	0.5750	4.50	7.82	
	0.44375	3.275	7.70	
	0.2500	1.875	7.50	7.04

Partition Coefficients of the Amines between Water and Ether.

Benzylamine	4.55	9.60	2.10	
	2.85	6.05	2.12	
	1.85	3.725	2.01	
	1.10	2.25	2.04	
	0.675	1.335	1.97	2.00
Benzylethylamine	0.92	12.92	14.1	
	0.56	7.60	13.6	
	0.365	4.995	13.7	
	0.230	2.83	12.3	
	0.145	1.74	12.0	11.6

	C_1	C_2	C_2/C_1	P
Benzylmethylamine	2.08	12.84	6.17	
	1.14	6.66	5.84	
	0.645	3.665	5.69	
	0.41	2.12	5.17	
	0.23	1.17	5.08	5.00
n-Butylamine	3.20	3.52	1.10	
	2.15	2.20	1.02	
	1.35	1.23	0.912	
	0.85	0.76	0.895	0.905
iso-Amylamine	0.8375	1.8375	2.19	
	0.4875	1.0125	2.08	
	0.3750	0.6500	1.73	
	0.2375	0.3875	1.63	2.02
Coniine	1.06	7.38	6.95	
	0.62	3.72	7.16	
	0.33	1.875	5.68	
	0.19	1.055	5.55	6.33
Diethylamine	7.9	6.3	0.798	
	2.875	2.025	0.704	
	1.650	1.075	0.652	
	1.100	0.7375	0.671	
	0.6125	0.4375	0.714	0.652
Diemethylamine	13.5	3.05	0.226	
	7.0	1.60	0.228	
	5.22	1.26	0.242	
	4.35	1.025	0.236	
	2.81	0.63	0.224	
	2.55	0.600	0.235	
	1.85	0.425	0.230	
	1.37	0.33	0.241	0.231
Dipropylamine	1.48	9.76	6.6	
	0.92	5.70	6.2	
	0.60	2.97	4.95	
	0.43	1.915	4.46	
	0.26	1.005	3.86	3.86

	C_1	C_2	C_2/C_1	P
Ethylamine	14.8	2.50	0.169	
	9.8	1.60	0.163	
	6.075	1.125	0.185	
	3.975	0.675	0.170	
	2.550	0.450	0.176	0.172
n- Heptylamine	0.385	8.00	20.8	
	0.275	5.145	18.7	
	0.200	3.105	15.5	
	0.120	1.41	11.75	10.3
Methylamine	34.5	3.9	0.113	
	19.1	2.05	0.107	
	11.25	1.225	0.109	
	7.60	0.90	0.118	
	4.90	0.575	0.117	0.113
-Methylpiperidine	5.92	10.92	1.85	
	3.42	6.20	1.81	
	2.065	3.59	1.74	
	1.33	2.31	1.74	
	0.805	1.37	1.70	1.68
Piperidine	17.85	14.10	0.790	
	11.30	8.60	0.760	
	6.70	4.85	0.724	
	3.80	2.60	0.685	
	1.675	1.10	0.657	0.655
Trimethylamine	9.90	6.30	0.707	
	4.45	3.00	0.675	
	2.65	1.775	0.670	
	1.775	1.1625	0.655	
	1.2125	0.800	0.660	0.660

BIOGRAPHY

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